

THE PRODUCTION OF SOLAR CELL GRADE SILICON FROM BROMOSILANES

FINAL REPORT

J. Schumacher
L. Woerner
E. Moore
C. Newman

JANUARY 1979

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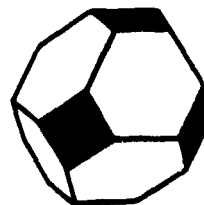
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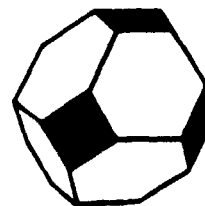
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FINAL REPORT

JPL Contract 954914

J. C. Schumacher, L. Woerner
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ABSTRACT

Based upon a chemical engineering analysis of existing semiconductor grade polycrystalline silicon processes, Cost Element Objectives for (1) Capital Equipment, (2) Raw Materials, (3) Labor, and (4) Utilities were established to meet the LSA Project Silicon Materials Task Cost Objective of \$10/kg for Solar Cell Grade(SCG) Silicon. A continuous Flow Reactor (CFR) process based on the hydrogen reduction of the bromosilanes SiBr_4 and SiHBr_3 was proposed by the J. C. Schumacher Company to meet these Cost Element Objectives, which resulted in the letting of JPL Contract 954914 to the Company. Initial experiments carried out as part of this contract, directed at obtaining overall yield data for bromosilane reduction in the CFR, indicated the need for increased reactor residence time and deposition substrate particle packing density to fully characterize the kinetics (rate) and thermodynamics (yield) of observed silicon production. Fluidized bed experiments were therefore initiated to overcome these experimental difficulties, which showed both thermal decomposition and hydrogen reduction of SiHBr_3 in a fluid bed reactor to present attractive closed-loop processes for producing SCG polycrystalline silicon consistent with Cost Element Objective derived earlier. No process selection could be made however due to the fact that preliminary optimization of 2 of 3 process stages in each case during the course of the experimental program showed comparable attainment of Cost Element Objectives. Further experiments to complete process selection and preliminary process economic evaluation and design are therefore suggested.

1.0 INTRODUCTION

1.1 Foreword

This Final Report is submitted by the J. C. Schumacher Company in partial fulfillment of the requirements of JPL Contract No. 954914. The work described herein was performed during the period 10/24/77 to 11/9/78, as part of the Silicon Materials Task of the Low-Cost Solar Array Project. Contributors to the work performed were:

- o John C. Schumacher; Project Manager
- o Lloyd Woerner; Principal Investigator
- o Edward Moore; Project Engineer
- o Charles Newman; Research Scientist

J. C. Schumacher Company efforts during the life of Contract No. 954914 were directed by the Contract Statement of Work at "conducting the initial phase of a program to determine the feasibility of a high velocity, gaseous-reaction process for the hydrogen reduction of bromosilanes utilizing a continuous-flow reactor having continuously-introduced particles, which act as silicon deposition substrates, that are mixed with and conveyed by high-velocity gaseous reactants through the reaction zone and terminate in a continuous discharge for the low-cost, high-volume production of solar grade silicon."

In particular, tasks to be performed during the first program phase would establish detailed overall yield data suggested by, but not actually available in, the literature upon which feasibility of the proposed approach depended.

An experimental program was therefore initiated to obtain the requisite yield information, for hydrogen reduction of silicon tetrabromide (SiBr_4) and tri-bromosilane (SiHBr_3) in a high velocity continuous flow reactor (CFR) which utilized Si particles as the product deposition substrate.

1.2 CFR Studies

As originally conceived, the CFR involved separate pre-heating of the reactants H_2 , and SiBr_4 or SiHBr_3 , and the deposition substrate Si particles, and their coaxial, cocurrent injection into the reaction zone. Small-scale equipment design and materials of construction (quartz), however, precluded obtaining sufficient reactor residence time at temperature to generate meaningful reaction rate and yield data in the initial experiments which employed SiBr_4 . Countercurrent substrate injection and fluid bed experiments were, therefore, initiated to obtain actual

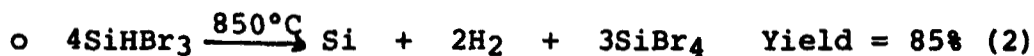
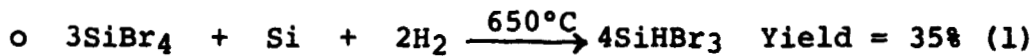
rate and yield data for both SiBr_4 and SiHBr_3 , in the temperature ranges of interest.

1.3 Fluid Bed Reactor Experiments

1.3.1 Candidate Closed Loop Processes

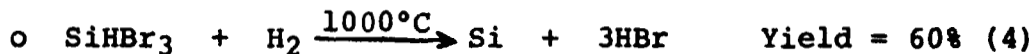
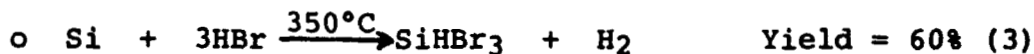
Fluid bed experiments carried out with SiHBr_3 , showed two processes based on a fluid bed reduction stage to have exciting potential for meeting Silicon Materials Task cost objectives, resulting from apparent advantages of SiHBr_3 over SiHCl_3 . The processes were as follows:

Thermal Decomposition Process



and

Hydrogen Reduction Process



1.3.2. SiHBr_3 Process Advantages vs SiHCl_3

Apparent advantages of the SiHBr_3 system over the SiHCl_3 system found during the experimental investigation were:

(1) Inhibited Homogeneous Nucleation During Thermal Decomposition

It is well known (1) that SiHCl_3 undergoes low temperature thermal decomposition in the 700°C to 1100°C temperature range. A viable ultrahigh purity silicon production process has, however, not been able to be developed utilizing this scheme due to the tendency for the reaction product silicon to homogeneously nucleate in the vapor phase producing a fine (1 micron) particle, amorphous product. High temperatures (1250°C) and a large excess (20/1) of hydrogen in a hydrogen reduction process are in fact required to suppress the observed tendency of the SiHCl_3 system for homogeneous nucleation.

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Homogeneous nucleation has been found with the SiHBr_3 system only under low temperature ($700^\circ\text{C} - 800^\circ\text{C}$) and very short residence time (.1 - .2 sec.) conditions, so that thermal decomposition at low temperature ($800^\circ\text{C} - 850^\circ\text{C}$) becomes a feasible process. The low temperature and elimination of the large excess hydrogen requirements are obvious advantages of this process.

(2) Absence of Wall Deposition

Wall deposition has been found to be only minimal in thermal decomposition of SiHBr_3 .

(3) Absence of Polymer Formation

Formation of explosive polymer is well known in SiHCl_3 hydrogen reduction by the Siemens Process. No polymer formation has been observed in extensive thermal decomposition or hydrogen reduction of SiHBr_3 .

(4) Large Particle Production

Thermal decomposition of SiHBr_3 yielded a large dense particle product (250 to 350 microns) from an 80 mesh (170 micron) fluid bed due to the absence of homogeneous nucleation. Obvious product handling advantages result. The hydrogen reduction process product has not been fully size analyzed at present, but was similar in appearance.

As a result of the success of the SiHBr_3 fluid bed experimental investigations, the focus of JPL Contract No. 954914 was changed from obtaining bromosilane hydrogen reduction kinetic data in the CFR to establishing which process, (1) the Thermal Decomposition Process, or (2) the Hydrogen Reduction Process, presented the more attractive opportunity for economic exploitation in terms of meeting Silicon Material Task cost reduction objectives.

1.4 Processes for Continued Study

Both the Thermal Decomposition Process and the Hydrogen Reduction Process which employ SiHBr_3 to produce SCG polycrystalline silicon present attractive opportunities for meeting LSA Project Silicon Materials Task cost objectives. This can be inferred from simple estimates of about \$15,000,000 for Capital Equipment for both processes presented below, which are shown through Cost Element Analysis to be consistent with overall cost objectives.

Further study of both processes is, however, required for process selection. Each process consists of three basic elements, one of which (purification) is common. Studies carried out to date have largely been confined to the common stage as well as the final (decomposition) stage of the Thermal Decomposition Process, and the initial (SiHBr_3 Synthesis) stage of the Hydrogen Reduction Process, due to the need to first demonstrate feasibility of the SiHBr_3 approach. Thus, though overall feasibility of both processes has been shown, additional experiments are suggested to optimize both processes in their complete form. Process selection will then be made on the basis of the optimized overall process.

2.0 BACKGROUND

2.1 The LSA Project Silicon Materials Task

Although many questions exist at present concerning the exact details of how photovoltaic electric generating capacity will be integrated into existing distribution networks, and to what extent it will impact future energy supply requirements, both industry and government agree that meaningful contributions will be made by this technology, when and if installed generating capacity capital costs can be reduced from the present level of \$15/watt to the order of \$1/watt.

The U.S. Department of Energy is, therefore, supporting achievement of this cost reduction objective through financing a number of R&D and "market pull" programs, among which is the Low-Cost Solar Array (LSA) project directed and administered by the Jet Propulsion Laboratory of the California Institute of Technology (JPL). LSA Project goals include a price of less than \$0.50/(peak) watt by 1986 for installed Silicon Solar Cell photovoltaic electric generating capacity.

To achieve LSA project overall cost reduction goals, JPL has organized several individual tasks directed at reducing individual cost elements of installed photovoltaic electric generating capacity. Among these individual tasks is the Silicon Materials Task, which has the objective of reducing the cost, both in terms of dollars and energy investment, of the ultrahigh purity polycrystalline silicon ("poly") used in silicon solar cell fabrication from the present level of \$60 and 500 KWH/kilo to less than \$10/kilo.

JPL Contract 954914 was let to the J.C. Schumacher Company as part of the Silicon Materials Task of the LSA project.

Given the task of reducing "poly" costs from \$60 and 500 KWH per kilo to less than \$10/kilo, existing production processes first were examined to delineate those process steps with the greatest probability of cost reduction success.

2.2 Existing Polycrystalline Silicon Production

The poly used currently in silicon solar cell fabrication is Semiconductor Grade (SG) polycrystalline silicon developed for use in integrated circuit manufacture. For LSI and VLSI integrated circuit manufacture, SG poly must have an extremely low concentration of alkali, alkaline earth and first transition series metals (10 parts per billion total electrically active species), as well as a low defect concentration. The physics of device property effects, including minority carrier lifetime, of these impurities (both metals and defects) is identical in both sophisticated integrated circuits and photovoltaic solar cells (a simple deep junction large area diode). However, device packing density is much greater in IC fabrication so that it is possible that poly used in solar cell fabrication Solar Cell Grade (SCG) poly, can have a considerably increased impurity concentration specification as a means of reducing manufacturing costs. This point is under separate study as part of the LSA project, and SCG poly continues undefined. Specific cost reduction approaches based on loosening impurity concentration specifications are, therefore, not possible at this time, and the basic SG Silicon process must be improved to achieve the desired objectives.

In brief, SG poly is today produced by the Siemens Process(2) in which metallurgical grade (MG) silicon is reacted with HCl in the presence of a copper catalyst to form trichlorosilane (SiHCl_3) which is purified by distillation and subsequently reduced in a 20/1 excess of hydrogen at 1200°C and deposited on a hot, high-purity silicon filament in a CVD ("C") reactor. Low yields and high energy use occur in all process steps as well as low throughput rate in the CVD stage. Separation and recycle of by-products place additional serious limitations on the process.

2.3 Existing Process Cost Estimate

An estimate of the present manufacturing cost can be made with the aid of simple chemical engineering estimating rules as follows. Starting with a selling price of \$60/kg, and factoring the items of general expense, a manufacturing cost of \$27.60/kg can be derived as shown in Table 1.

TABLE 1
ESTIMATION OF MANUFACTURING COST
FROM SELLING PRICE

Selling Price (SP)		\$60.00/Kg
Less:		
Selling Expense	@ 5% of SP =	3.00
General and Admin.	@ 10% of SP =	6.00
R & D	@ 4% of SP =	2.40
Gross Profit	30 to 40% of SP =	18.00 to 24.00
e.g., Taxes	@ \$9.00 to \$12.00	
Net Profit	<u>\$9.00 to \$12.00</u> *	_____
Total	\$18.00 to \$24.00	
	Sub Total	29.40 to 35.40
Net Equals Manufacturing Cost =		\$24.60 to 30.60
	Average	\$27.60

* Net profit of \$9 to \$12 (Ave \$10.50) is equivalent to about 17 per cent of selling price, which is not unreasonable in a highly technical, high risk business.

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TABLE 2
BREAKDOWN OF ESTIMATED
MANUFACTURING COST INTO ELEMENTS

<u>COSTS</u>	<u>(a)</u> <u>\$/Kg</u>	<u>(b)</u> <u>\$/Kg</u>
Direct Costs		
Raw Materials	\$ 4.50	\$16.87
Labor Approx. 52 men @ \$5/Hr.	4.60	4.02
Supervision @ 25% of labor	1.15	0.60
Utilities:		
Electrical 500 KWH @ 0.7 KWH	3.50	9.64
Maintenance (7.5% of Capital Cost Annually)	3.01	2.38
Plant Supplies (14% of Maintenance)	0.42	0.48
Royalties (2.5% of Mfg. Cost) * (By-product credit)	0.69	(6.85)
TOTAL DIRECT COSTS	\$17.87	\$27.14
Indirect Costs		
Payroll Overhead 15% of Labor	\$ 0.69	\$ 5.50
Laboratory 20% of Labor	0.92	0.60
Plant Overhead 73% of Labor	3.35	4.20
TOTAL INDIRECT COSTS	\$ 4.96	\$10.30
Fixed Costs		
Depreciation (15 year straight line)	\$ 2.67	\$ 0.00
Taxes (2% of Capital Annually)	0.80	0.92
Insurance (3% of Capital Annually)	1.20	0.46
TOTAL FIXED COSTS	\$ 4.67	\$ 1.38
TOTAL MANUFACTURING COSTS	<u>\$27.50</u>	<u>\$38.82</u>

* Usually about 1-2% of Sales

(a) Factored estimates for Siemens Process based on methods presented by Aries and Newton (3).

(b) Detailed estimates for Siemens Process prepared by Carl Yaws (4).

Furthermore, using standard chemical engineering cost factors suggested by Aries and Newton (3), SC poly manufacturing cost elements can be derived, and are shown in Table 2. Also shown in Table 2 are the detailed estimates of SG poly manufacturing cost elements prepared by Carl Yaws of Lamar University (4) as part of the Silicon Material Task. These detailed estimates validate the estimating factors presented in (3).

2.4 Manufacturing Cost Element Analysis

The Aries and Newton manufacturing cost estimate analysis bases cost elements on 4 independent variables:

- (1) Raw Materials
- (2) Operating Labor Cost
- (3) Utility Cost
- (4) Capital Cost

If we symbolize these various quantities as follows:

M	=	manufacturing cost
RM	=	raw material cost
L	=	operating labor cost
U	=	utility cost
K	=	capital cost (in millions of dollars)
R	=	production rate (in millions of kg/yr)

then

K/R = Capital cost expressed as dollars per kg of annual production.

All other cost elements of M are a function of these independent variables.

From Table 2 we can see that manufacturing cost can be expressed as

$$M = 2.33 L + .2025K/R = RM + U \quad (5)$$

if royalties are ignored.

Cost estimates presented in Table 2 were developed as follows with the aid of equation (5):

- o M = \$27.60, from Table 1
- o U = 500 KWH/kg based on T^4 radiation losses in the "C" reactor and the known thermodynamics of SiHCl_3 synthesis and distillation.
- o L = 52 operators; chemical engineering experience
- o RM = based on 98% synthesis yield, 50% distillation yield, and 55% hydrogen reduction yield where yields include recycle recovery, and MG Si at \$.6/kg, Cl_2 at \$.1375/kg, and H_2 at \$2.00/kg.

2.5 Process Cost Element Objectives

Utilizing the validated equation (5), some guidelines for a process which would meet Silicon Material Task objectives could next be drawn.

- o The existing labor force of 52 operators for 500,000 kg/year production can, with automation and continuous operation reasonably be expected to be halved while doubling production. Thus,
 $L = \$4.60/4 = \$1.15/\text{kg}$ and $2.33 L = \$2.68/\text{kg}$
- o The utilities cost must be reduced from \$3.50/kg to about \$1/kg by elimination of the "C" reactor in the reduction stage.
- o A capital cost of \$20,000,000 for 1,000,000 kg/year production would add \$4.20/kg to manufacturing costs (0.2025 K/R) so that \$15,000,000 capital invested maximum, or \$3.04/kg in capital related costs is a necessary objective.
- o In a closed-loop process with 100% yield and total recycle, raw material costs are a minimum at \$0.6/kg.

Setting manufacturing cost at \$8/kg and utilizing the guidelines just suggested, the plant meeting Silicon Material Task objectives can be defined with the aid of equation (5) as:

			\$/kg
L	=	\$ 1.15	L = \$2.68
U	=	\$ 1.00	U = \$ 1.00
CAPITAL	=	\$15,000.000	0.21K/R = \$ 3.04
RATE	=	1,000,00 kg/yr	
R.M.	=	\$ 1.17/kg	R/M = <u>\$ 1.28</u>
M	=		= \$ 8.00

Detailed cost elements are presented in Table 3.

TABLE 3

REPRESENTATIVE MANUFACTURING COST ELEMENTS
TO MEET PRODUCTION COST GOALS

Capital Cost = \$15 million

<u>Direct Costs</u>	<u>\$/kg</u>
Raw Material	1.28
Labor	1.15
Supervision	0.29
Utilities	1.00
Maintenance	1.13
Plant Supplies	<u>0.16</u>
TOTAL DIRECT COSTS	5.01
<u>Indirect Costs</u>	
Payroll Overhead	0.17
Laboratory	0.23
Plant Overhead	<u>0.84</u>
TOTAL INDIRECT COSTS	1.24
<u>Fixed Costs</u>	
Depreciation	1.00
Taxes	0.30
Insurance	<u>0.45</u>
TOTAL FIXED COSTS	1.75
TOTAL MANUFACTURING COSTS	8.00/kg

2.6 Proposed SCG Polycrystalline Silicon CFR Process

A high velocity, continuous-flow reactor (CFR) process for the hydrogen reduction of bromosilanes, utilizing separately preheated and injected silicon particles as deposition substrates, was proposed by the J. C. Schumacher Company to meet Silicon Material Task cost objectives. This concept was developed in the following way.

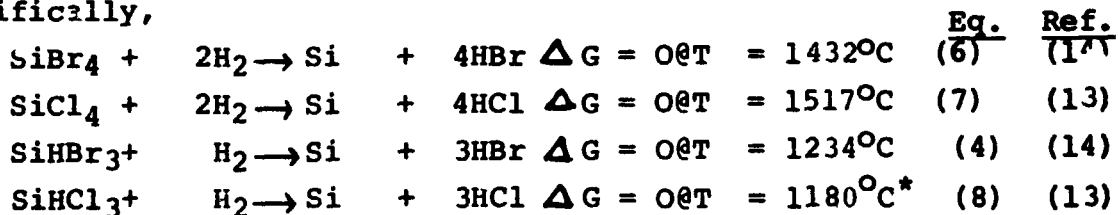
The hydrogen reduction of SiBr_4 or SiHBr_3 has a negative Gibbs Free Energy at roughly 900°C - 1050°C (see below). Economic production of solar cell grade silicon with this system is, therefore, a matter of nucleation and growth kinetics. Bertrand and Olsen recognized this point in their patent (5) covering processes for reduction of halosilanes in fluid bed reactors. In this reference, the authors present numerous examples including $\text{SiBr}_4\text{-H}_2$ system data suggesting favorable kinetics. They go on, however, to point out that the fluid bed need not be static, but can be conveyed through a long tubular reactor at high velocities to effect the desired result. No data on this particular approach are presented, but it is interesting to speculate that the concept was derived from earlier work performed by Olsen on TiO_2 formation in a "burner type" reactor (6).

Reactant temperature, substrate particle size and linear velocity of reactants are the variables to be adjusted to optimize the economics of silicon production in this manner. Candidate design concepts for the reactor could be drawn from the TiO_2 production experience reflected in (7) through (10). Reference (11) describes a fluid bed reactor design for TiO_2 production which did not achieve commercialization, while (12) cites the beneficial effect of very high gas velocities in CVD reactors.

Thermodynamic and kinetic data available in the literature and elsewhere bearing on the proposed CFR hydrogen reduction of bromosilanes were as follows:

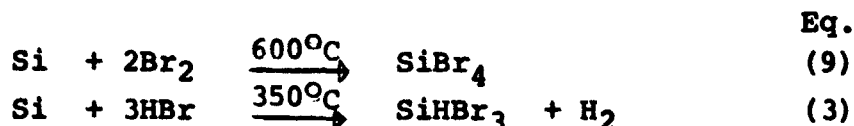
2.6.1 Thermodynamics

Thermodynamic property estimates for the Si-H-Br system by Hunt and Sirtl (13) and Miller and Grieco (14) indicated that the temperatures at which hydrogen reduction reactions developed a negative free energy were 150°C to 200°C lower for bromosilanes than for analogous chlorosilanes. Specifically,



* see Appendix

Additional utilities cost reductions would result from the proposed SiBr_4 and SiHBr_3 low temperature synthesis processes described in (15).



2.6.2 Kinetics

Hunt and Sirtl (13) report the qualitative observation that bromosilane hydrogen reduction proceeded at about 1.5 times the rate of the analogous chlorosilane. In addition, silicon tetrabromide synthesis carried out by the J. C. Schumacher Company according to equation (9) in company sponsored research programs aimed at CVD source material product development showed greater than 90% yield at 1 kilo/hr-in² and residence times of .1 to .4 seconds in a static uncatalyzed bed. Thus, an identical process to that presently used for SG poly production, employing bromosilanes instead of chlorosilane, because of improved reaction rates, would require 2/3 or less capital contribution, if Hunt and Sirtl's observations proved correct.

2.6.3 Physical Properties

It is well known from the work of Sangster (16) that the bromosilane system presents more advantageous partition coefficients for purification across the liquid-vapor phase boundary, than the chlorosilane system. This has also been established in J. C. Schumacher Company sponsored research where 1/3 less theoretical plates are required to achieve equal product purities in bromine compounds of boron, phosphorus, and silicon than the corresponding chlorine analogs. This factor also would be expected to significantly reduce capital contributions to manufacturing cost.

In summary then, the process proposed for investigation by the J.C. Schumacher Company under JPL Contract No. 954914 was based on:

- (1) Use of SiBr_4 or SiHBr_3 rather than SiHCl_3 . Increased raw material acquisition costs ($\text{Cl}_2 = \$0.1375/\text{kg}$ vs. $\text{Br}_2 = \$0.55/\text{kg}$) would be offset by complete recycle to hold net raw material cost in the range of \$1.50 to \$2.00/kg product.
- (2) Synthesis and purification of the bromosilane chosen in a manner similar to that used in the Siemens process although at a reduced capital cost contribution (from \$8.10/kg to \$3.15 overall) based on anticipated improvements in yield, rate and partition coefficients in these operations.

- (3) Replacement of the SiHCl_3 "C" reactor hydrogen reduction process stage with the CFR hydrogen reduction of bromosilane, to complete the capital and operating cost reductions. The proposed CFR was based on existing TiO_2 process equipment in which SiHBr_3 or SiBr_4 and H_2 would be separately preheated and then introduced into a long horizontal tube reactor where they were mixed with hot silicon particles introduced to both act as a Si growth substrate and to scour the reactor walls of product deposited there. The reactor was proposed to be a high-velocity continuous-flow reactor with total by-product separation and recycle.

Inasmuch as only qualitative kinetic data were available concerning hydrogen reduction of bromosilanes, the process development program was proposed in several phases, with review and decision at the conclusion of each phase. The initial program phase proposed to investigate preliminary feasibility of the approach by determining the CFR overall yield data of hydrogen reduction of SiBr_4 and SiHBr_3 in the CFR.

3.0 INITIAL EXPERIMENTS

3.1 General

As mentioned previously, the continuous flow reactor (CFR) proposed for hydrogen reduction of bromosilanes was based on an analogous process utilized for commercial production of TiO_2 (6). This process involves separate preheating of reactants to a temperature where the desired reaction free energy is negative, followed by reactant stream mixing and seeding with nucleation and deposition substrate particles. The experimental program designed for preliminary evaluation of feasibility of the proposed CFR process consisted of:

- o Obtain data on the yields of the reactions involved.
- o Determine the distribution of silicon product in its various forms: (1) deposit on seed particles; (2) deposit on reactor walls; and (3) fine particles.
- o Investigate the effect of the pertinent reaction parameters, such as temperature, residence time, stoichiometry, gas stream velocity, and rates of heating and cooling, on the yields of the various products and their forms, with the goal of maximizing deposition of silicon on the seed particles, and minimizing formation of undesirable fines. Both the inlet and outlet compositions are to be determined as functions of time. The axial temperature profile in the reactor is to be measured.
- o Obtain mass and energy balances with sufficient accuracy to allow evaluation of the process.
- o Conduct a series of approximately three demonstration runs to demonstrate the process.
- o The silicon product produced in the demonstration runs, packaged separately by run, shall be supplied to JPL. Silicon products from other experiments performed in the course of the Contract shall be supplied to JPL upon request by JPL.

An experimental apparatus (described below) was, therefore, designed and constructed based on the teachings of (6) through (11). Preheating studies in this apparatus were then carried out to establish attainment of the required temperature (1100°C), and experiments initiated to determine rate and yield of hydrogen reduction of SiBr_4 in the CFR. Table 4 presents SiBr_4 and SiHBr_3 physical property data.

Preheating studies established thermal stability of SiBr_4 to 1100°C and the design of a 4-pass quartz heat exchanger which allowed attainment of an 1100°C H_2 temperature. Little (2-3% per pass) reduction of SiBr_4 to Si was obtained because of short reactor residence times at temperatures greater than that at which negative reaction free energy occurs. These experiments are described below under Cocurrent CFR Studies.

Theoretical studies were then initiated to establish residence times required for meaningful particle growth, which showed times of the order 0.1 to 0.3 second to be necessary. These calculations are summarized below under Kinetic Analysis.

It was determined that the residence times required for meaningful particle growth could be obtained either in a countercurrent CFR or in a fluidized bed reactor. Both were designed and constructed but the countercurrent CFR reactor presented experimental difficulties while the fluidized bed showed exciting promise for meeting program objectives. Efforts were thereafter concentrated on the fluidized bed reactor approach.

The Countercurrent CFR Studies are briefly discussed below while the Fluidized Bed Studies results and projections are the subject of Sections 4.0 and 5.0.

3.2 Cocurrent CFR Studies

Figure 1 presents a schematic layout of the experimental apparatus. Preheaters consisted of 4 passes of 10mm O.D. quartz tubing which were maintained in temperature ambients up to 1350°C by a Lindberg diffusion furnace. The reactor itself was constructed of 25mm O.D. quartz tubing, while the cyclone separator and auxiliary condensers were Pyrex. SiBr_4 was used as the silicon source material.

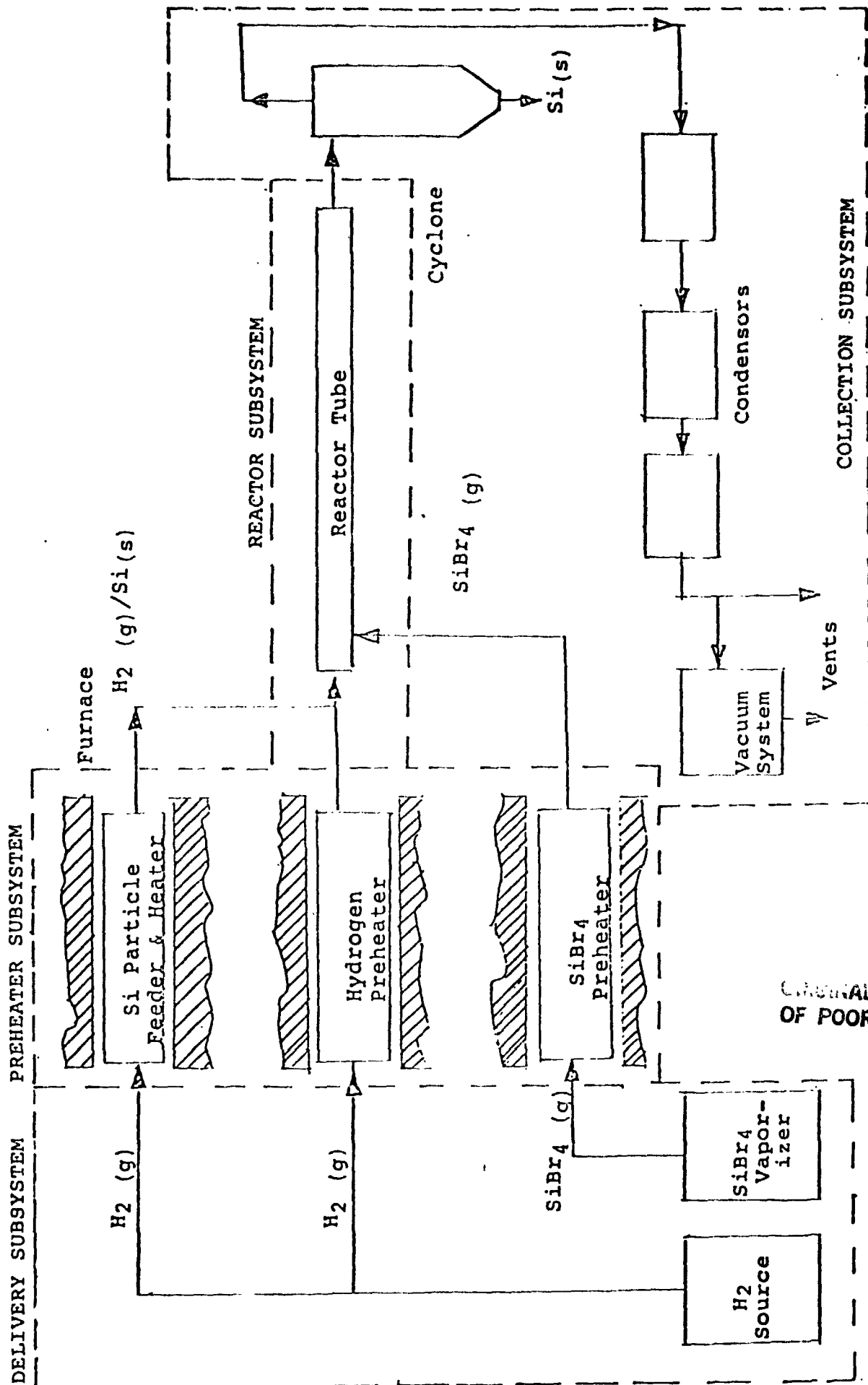


FIGURE 1. REACTION SYSTEM SCHEMATIC

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TABLE 4

PROPERTIES OF TRIBROMOSILANE
AND TETRABROMOSILANE

A. TRIBROMOSILANE:

Mole Weight:	269 grams (rounded)
Boiling Point:	109-111°C
Freezing Point:	-73°C
Density:	2.7 g/ml

It is a colorless corrosive liquid which spontaneously ignites in air, burning with an orange-white flame; it reacts with moisture producing HBr and hydrated silica. It is very corrosive toward stainless steel grades 304, 316, and 321. Has a pronounced tendency to cause standard taper and ball and socket ground joints to freeze. Reacts with most rubber, silastic, and plastic materials. Teflon appears to be stable towards it, but it is not known if teflon contaminates it. Fires can readily be extinguished with H₂O or by blanketing a spill with an inert gas such as N₂ or Ar.

B. TETRABROMOSILANE:

Mole Weight:	348 grams (rounded)
Boiling Point:	154°C
Freezing Point:	5°C
Density:	2.8 g/ml

It is a colorless liquid, which often has an orange hue due to the presence of free bromine, which hydrolyzes in moist air to HBr and hydrated silica. It is very corrosive to stainless steel grades 304, 316, and 321. It reacts with most rubber, silastic, and plastic materials. It has pronounced tendency to freeze ground joints similar to tribromosilane cited above. Teflon appears to be stable towards it.

Experimental results are presented in Table 5.

Initial runs, L1 through L5, showed the original nozzle type mizer design to produce excessive adiabatic expansion cooling of reactant streams. A "tee" type mizer was employed thereafter.

Runs L6 through L10 showed, as can be seen in Table 5, a finely divided brown reactor wall coating which was tentatively identified as amorphous silicon from its reaction with HF-HNO₃ etch. A white powder tentatively identified by color and melting point as Si₂Br₆ was isolated in the collection traps, along with large volumes of HBr. The quantity of HBr could not be accounted for by assuming it originated in formation of Si product obtained.

Preheated silicon particles were first introduced into the CFR in runs W1 through W3. Insignificant particle growth was observed, along with the same amorphous Si and Si₂Br₆ found previously, although the quantity of the latter was reduced. Little reaction of SiBr₄ was noted, and it was concluded that insufficient heat was being carried to the reactor by the reactant streams.

In runs W4 to W6, the reactor and mixer were, therefore, moved to within the furnace hot zone to create a hot wall reactor. No Si deposition substrate particles were employed. Polycrystalline silicon was uniformly deposited along the complete length of the reactor, while the reactant SiBr₄ was also partially converted to lower homologs and demonstrated by the density of collected silicon-bearing liquids of 2.6 gm/cc (compared to an SiBr₄ density of 2.8) and the spontaneous ignition in air of the higher boiling fractions of these liquids. (SiHBr₃ is known to spontaneously ignite in air.)

Runs W7 and W10 repeated the conditions of the previous experimental set, except that silicon particle deposition substrates were injected in the hydrogen stream to the hot wall reactor. Approximately 2-3% weight gain of the mean injected particles was observed while the particle diameter increased 4 microns from 66 to 70. Additionally, the mean mass diameter of the injected particles was shifted from 297 to 370 microns. The mean mass diameter is defined as the particle diameter below which 50% of the total mass occurs. Wall deposition and partial SiBr₄ reduction to lower homologs was again noted.

FOLDOUT FRAME

TABLE 5

RUN CONDITIONS - COCURRENT CFR STUDIES

<u>RUN NO.</u>	<u>REACTOR TEMP °K</u>	<u>PRESSURE TORR</u>	<u>MOLES H₂/ MOLES SiBr₄</u>	<u>PARTICLE RATE G/MIN.</u>	<u>NOTES</u>
Nozzle/Mixer					
L-1	1012	200	38	--	Fog formed in Liquid cyclones Small amount of solid in the recovery system
L-2	1022	200	33	--	Same as L-1
L-3	1030	200	28	--	Same as L-1
L-4	1025	760	34	--	Same as L-1
L-5	1030	Run aborted; failure of hydrogen preheater.			
Tee configuration for mixing.					
L-6	1354	760	9.4	--	White, finely collected divided reactor
L-7	1331	760	8.7	--	Same as L-6
L-8	1344	760	6.7	--	Same as L-6
L-9	1300	760	15	--	Same as L-6
L-10	1330	760	12	--	Same as L-6
W-1	1341	760	15.5	0.86	Fog or finely formed introduced finely colored
W-2	1373	760	8.0	1.5	Same as W-1
W-3	1353	760	12		

L-10	1330	760	12	--	Same as L-6, above
W-1	1341	760	15.5	0.86	Fog or finely divided white solid formed. Recovery of silicon introduced was nearly complete. Some finely divided brown-to-cream colored material recovered.
W-2	1373	760	8.0	1.5	Same as W-1, above
W-3	1353	760	12	2.7	Same as W-1, above
W-4	1319	760	17	--	Wall deposition in reactor. Some lower homologs captured. Reduction in volume of finely divided white solid.
W-5	1325	760	17	--	Same as W-4, above.
W-6	1320	760	17	--	Same as W-4, above
W-7	1333	760	18	2.2	Heavy wall deposition noted in reactor tube. Liquids in traps had densities which differed from starting material. HBr and lower homologs collected in traps.
W-8	1325	760	16	2.1	Same as W-7, above
W-9	1330	760	17	2.0	Same as W-7, above
W-10	1290	750	17	3.5	Same as W-7, above

FOLDOUT FRAME

2

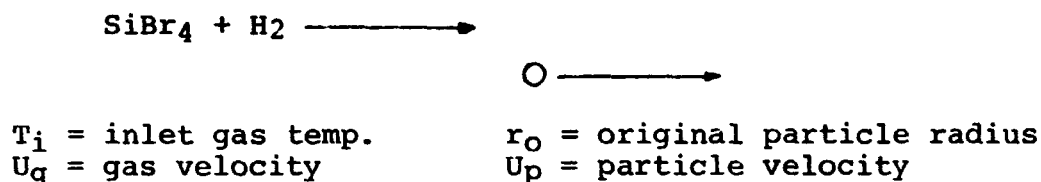
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It was, therefore, concluded that the hydrogen reduction of SiBr_4 at about 1025°C to 1050°C , and deposition of the product silicon on separately preheated and injected silicon particle deposition substrates, would be feasible if residence times at this temperature could be increased. A theoretical analysis was undertaken to establish residence time requirement guidelines.

3.3 Kinetic Analysis

The intent of the calculations summarized here was to establish the order of magnitude of the residence times required in the CFR at reaction temperatures to obtain meaningful particle growth. Professor William A. Tiller of Stanford University, Materials Science Department, performed the calculations.

The model system considered was as follows:



It was desired to calculate the one-dimensional growth rate \dot{r} for silicon particles of initial radius r_o in a $\text{SiBr}_4 + \text{H}_2$ gaseous environment at T_i inlet gas temperature, accounting for particle heat loss due to silicon deposition from the gas stream and due to convection, while ignoring wall effects. \dot{r} was considered to be a function of initial particle radius r_o , particle-gas differential velocity $U_\infty = U_g - U_p$, inlet gas temperature T_i , particle-inlet gas temperature differential ΔT_{ip} , and the Br/H ratio. Thus,

$$\dot{r} = f(r_o, U_\infty, T_i, \Delta T_{ip}, \text{Br/H}) \quad (10)$$

Matter transport could then be modeled by boundary layer analysis techniques detailed by Levich (17).

$$\dot{r} = 2 \Omega N_{\infty i} D_i^{2/3} U_{\infty}^{1/3} r^{-2/3} \quad (11)$$

where

Ω = Silicon solid atomic volume

$N_{\infty i}$ = Concentration of i^{th} species at the outer boundary layers

D_i = Diffusion coefficient i^{th} species in the boundary layer.

Heat transport could similarly be expressed, with the assumption that thermal diffusion precludes thermal gradients within an individual particle, as

$$\Delta \dot{T}(d) = \frac{3(\Delta H_d)}{C_p} \frac{\dot{r}}{r_o} = \text{Particle heat loss rate due to deposition} \quad (12)$$

where ΔH_d = Heat of deposition/unit volume

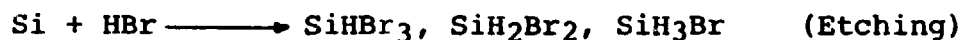
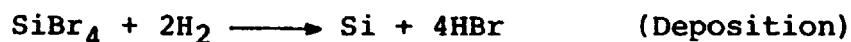
and

$$\Delta \dot{T}(c) = \frac{3K^*}{C_p} \frac{\Delta T_{ip}}{r\delta_t} = \text{Particle heat loss rate due to convection} \quad (13)$$

where K^* = Thermal conductivity of gaseous species

δ_t = Thermal boundary layer thickness

Thermodynamic contributions for the deposition and etching reactions



can, if interface equilibrium is assumed, be expressed for the j^{th} species is

$$K_j = \exp \left(\frac{-\Delta G^{\circ}_{Tj}}{R^*T} \right) \quad (14)$$

with ΔG°_{Tj} available from Hunt and Sirtl (13).

Diffusion coefficients can be calculated from gas dynamics where

$$D_j = 1/3 l_j V_j \quad (15)$$

where l_j = mean free path
 v_j = average particle velocity

and finally

$$K^* = C_v \bar{D}_j \quad (16)$$

Utilizing this model, it was then possible to calculate

$$\Delta \dot{T}(d) = 2.7(10)^3 \frac{\dot{r}}{r_o} \text{ } ^\circ\text{C/sec} \quad (17)$$

$$= 27^\circ\text{C/sec at } \dot{r} = 1 \text{ micron/sec and } r_o = 100 \text{ microns}$$

$$\Delta \dot{T}(c) = 4(10)^{-4} \frac{\Delta T_{ip}}{r_o} \quad (18)$$

$$= 4 \Delta T_{ip} ^\circ\text{C/sec at } r_o = 100 \text{ microns}$$

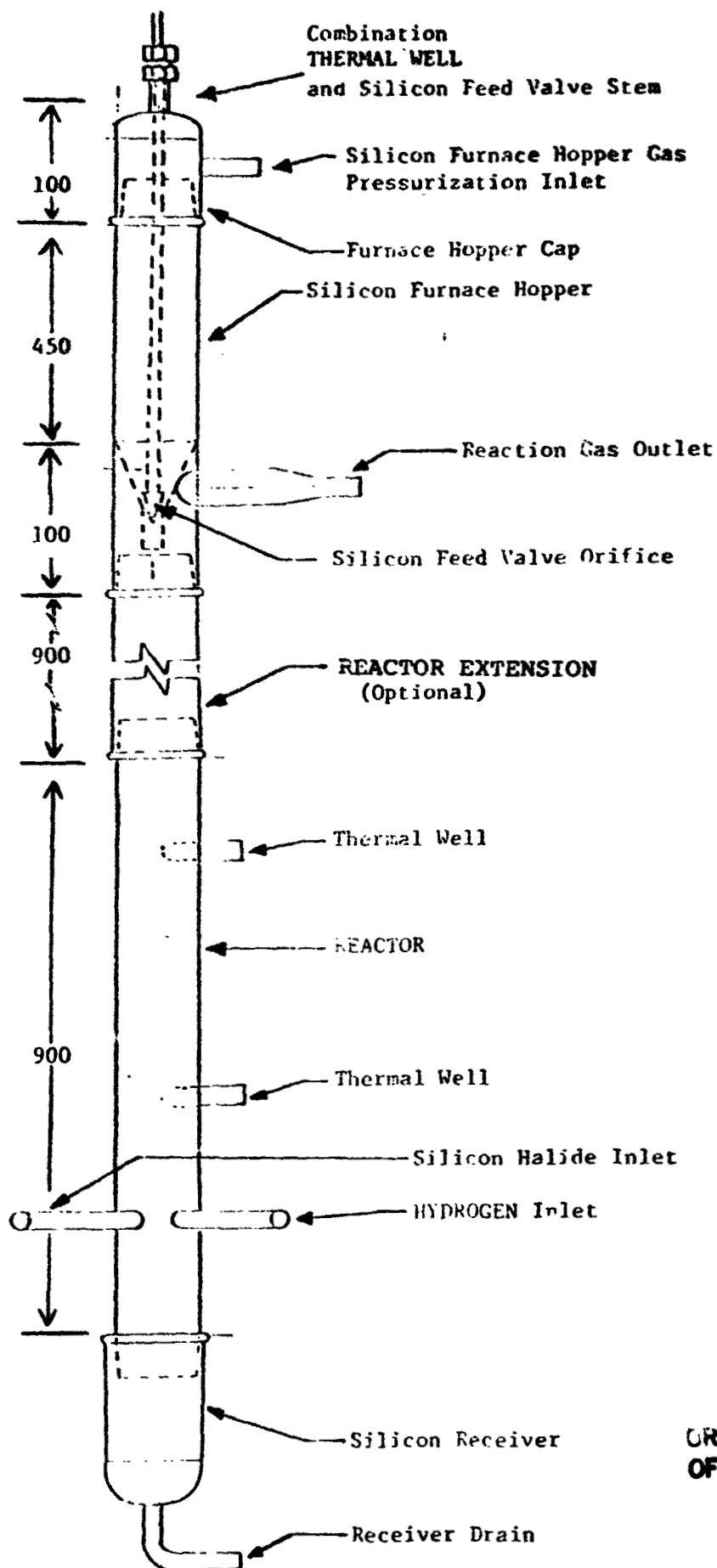
so that the following conclusions could be drawn

- (1) $\Delta T(c) \gg \Delta T(d)$
- (2) Any temperature differential between the gas stream and particle would disappear in 0.25 second maximum.
- (3) $\dot{r} = 1.4 \text{ micron/sec at } 1100^\circ\text{C}$

From these results, it was clear that multiple passes of particles through the reactant gas stream would be required to achieve meaningful particle weight increases. It was, therefore, decided to attempt to verify the theoretical conclusions in a countercurrent CFR and a fluidized bed reactor.

3.4 Countercurrent CFR Studies

Figure 2 presents a layout of the countercurrent CFR designed and constructed for verification of theoretical growth rates.



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FIGURE 2. COUNTERCURRENT REACTOR DESIGNED AND CONSTRUCTED FOR VERIFICATION OF THEORETICAL GROWTH RATES.

Experiments with this reactor were terminated after two runs. In the first, no conclusive results were obtained. In the second, feed particles were HBr etched in-situ prior to injection into the reactor with the result that they sintered into a solid mass. At this point, exciting results described below had been obtained with the fluid bed reactor and CFR studies were terminated.

4.0 FLUIDIZED BED REACTOR EXPERIMENTAL INVESTIGATIONS

4.1 General

The inability to produce significant amounts of silicon product in the previously described laboratory reactor configurations led to a series of experiments utilizing silicon seed particles in a fluidized bed reactor. Previous experiments demonstrated the production of silicon by the hydrogen reduction of tetrabromosilane; however, only slight changes in the total mass of the seed particles were obtained. Analysis of the reactor geometry, thermal profile, and reactant feed rates led to the following suppositions:

- (1) The seed particle density in the reaction zone was too low.
- (2) The residence time of reactants was too brief.

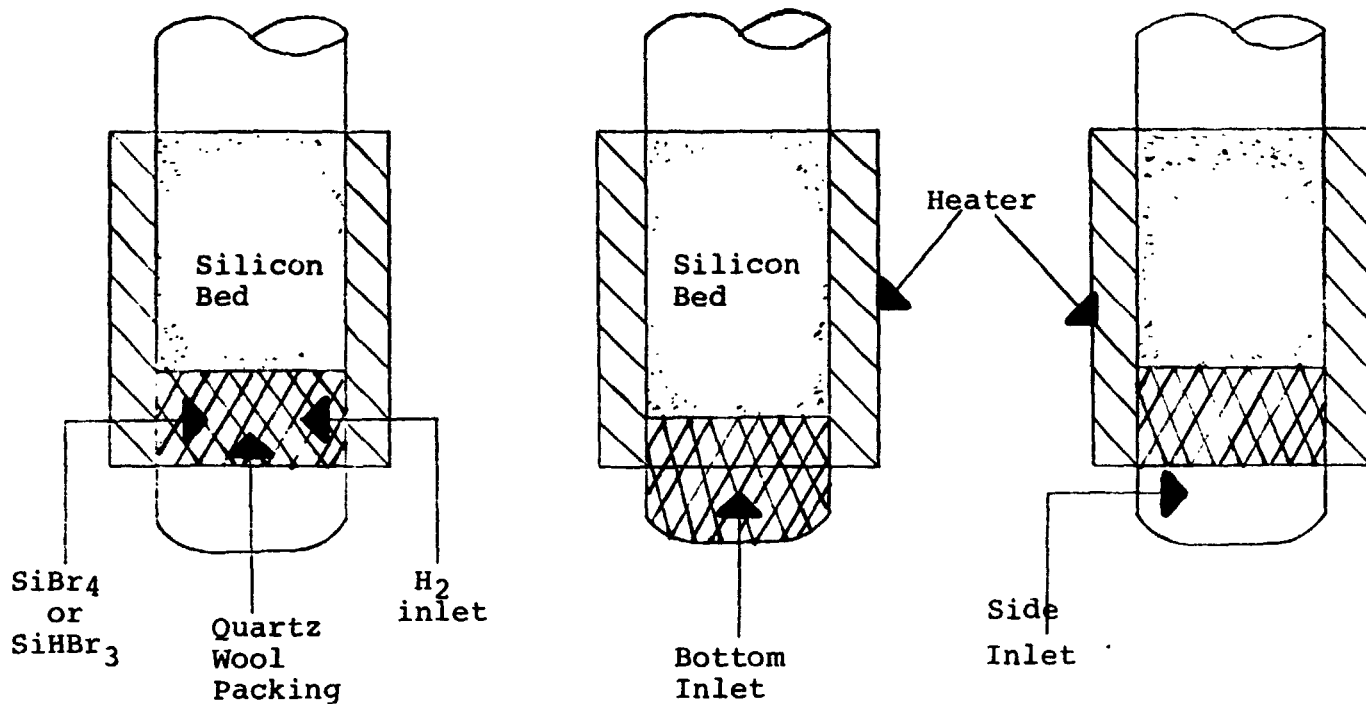
The fluidized bed reactor provided a convenient means of substantially increasing both the seed particle density and the residence time.

Initial fluid bed experiments used tetrabromosilane as the silicon precursor. These experiments yielded the unexpected results of a net loss of material from the silicon bed and the presence of a substantial amount of tribromosilane in the reactor effluent.

Subsequent experiments focused on the use of tribromosilane as the source for silicon. These later experiments yielded very promising results, both with and without the use of hydrogen as a reducing agent. The net results of the fluidized bed reactor experiments suggest the possibility of two separate and economically viable closed-loop processes for the commercial production of Solar Grade Silicon.

4.2 The Fluidized Bed Reactor

The countercurrent reactor (CCR), illustrated in Figure 2, was modified to serve as the fluidized bed reactor. The reactor, its various feed points and gas distributor configurations are illustrated in Figure 3. The fluidized bed reactor type was chosen as a device through which overall yield data could be obtained for the



MODIFICATIONS TO CCR
For initial fluid bed
experiments.

Single inlet configurations with
quartz wool gas diffuser in hot
zone of reactor

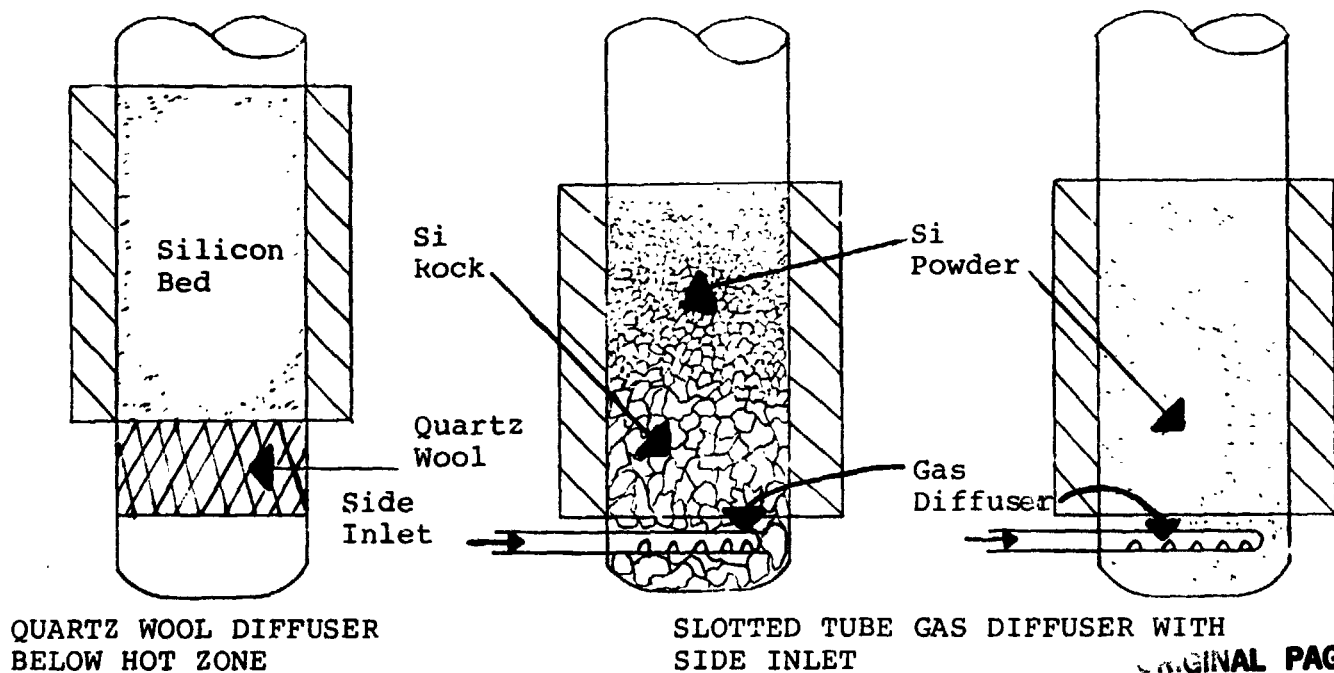
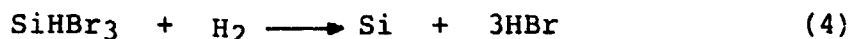
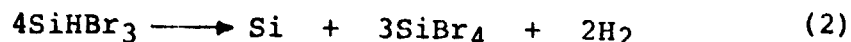
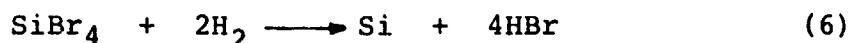


FIGURE 3

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FLUIDIZED BED REACTOR CONFIGURATIONS
USED IN HYDROGEN REDUCTION AND THERMAL
DECOMPOSITION EXPERIMENTS WITH SiBr₄
AND SiHBr₃

following silicon yielding reactions:



A detailed investigation and analysis of the operating and design parameters for fluidized bed reactors was not within the scope of this contract; however, certain well known operating parameters were used to characterize the experimental results. These include:

- (a) C_A concentration of gas A, gmol/cm^3
- (b) d_p particle diameter, cm
- (c) d_t reactor diameter, cm
- (d) h static height of bed, cm
- (e) L_f height of bubbling fluidized bed, cm
- (f) U_0 superficial fluid velocity through reactor, cm/s
- (g) τ average residence time of reactive species in fluidized bed based on superficial fluid velocity, s
- (h) T_r average temperature of fluidized bed, $^\circ\text{C}$

The reactor, bed, and particle dimensions were directly measured prior to each experimental test. The reactant concentration, superficial velocity, and average residence times were calculated on the basis of the flow, pressure, and temperature measurements made during the experiment. Example calculations follow:

Concentration of reactant A in feed, C_A

Data Required

P_s = System pressure = 770 mm Hg

T_s = reactant source temperature = 335°K

P_A^* = vapor pressure of reactant A at T_s = 150 mm Hg

Application of the ideal gas law gives,

$$C_A = \frac{P_A^*}{P_s} \times \frac{\text{gmol}}{22400\text{cm}^3} \times \frac{P_s}{760\text{mm Hg}} \times \frac{273^\circ\text{K}}{T_s} \quad (19)$$
$$= 7.18 \times 10^{-6} \text{ gmol/cm}^3$$

Superficial fluid velocity through reactor, U_o

Data Required

d_t = reactor diameter = 3.0 cm

L_f = height of bubbling bed = 12.5 cm

T_r = average temperature of fluid bed = 1075°K

T_a = ambient temperature = 298°K

G_a = gas feed rate to reactor measured at ambient temperature = 30cm³/s

P_s = system pressure = 770 mm Hg

P_a = atmospheric pressure

Application of the ideal gas law corrects G_a to conditions of temperature and pressure prevailing within the reactor.

$$\begin{aligned}
 G_{\text{corrected}} &= (G_a) \frac{(T_r)}{(T_a)} \frac{(P_a)}{(P_s)} \\
 &= 30 \text{ cm}^3/\text{s} \times \frac{1075^\circ\text{K}}{298^\circ\text{K}} \times \frac{760 \text{ mmHg}}{770 \text{ mmHg}} \\
 &= 107 \text{ cm}^3/\text{s}
 \end{aligned}
 \tag{20}$$

The superficial fluid velocity is computed as shown:

$$\begin{aligned}
 U_o &= \frac{G_{\text{corrected}}}{\pi \frac{d_t^2}{4}} = \frac{107 \text{ cm}^3/\text{s}}{\frac{\pi}{4} \times 3^2 \text{ cm}^2} \\
 &= 15.1 \text{ cm/s}
 \end{aligned}
 \tag{21}$$

Average residence time , τ

Data Required

$$\begin{aligned}
 d_v &= \text{reactor volume} = L_f \pi \frac{d_t^2}{4} \text{ cm}^3 \\
 &= 12.5 \text{ cm} \times \pi \frac{3^2 \text{ cm}^2}{4} \\
 &= 88.4 \text{ cm}^3
 \end{aligned}
 \tag{22}$$

$$\begin{aligned}
 \tau &= \frac{d_v}{G_{\text{corrected}}} = \frac{88.4 \text{ cm}^3}{107 \text{ cm}^3/\text{s}} \\
 &= 0.83 \text{ s}
 \end{aligned}
 \tag{23}$$

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4.3 Hydrogen Reduction of SiBr₄ in a Fluidized Bed Reactor

A series of experiments was conducted in a fluidized bed reactor to study the rate of production of silicon and the influence of such variables as reactor temperature, reactor feed rates, residence times, and the ratio of hydrogen to tetrabromosilane. The experimental apparatus is shown in Figure 4.

The hydrogen reduction of SiBr₄ to elemental silicon and hydrogen bromide at elevated temperature has been shown to be thermodynamically favorable for the reaction as written below at temperatures in excess of 1432°C [Equation (6)].*

Since $G = -RT \ln K$, where K is the equilibrium constant for the reaction, it is clear that K must be greater than unity whenever G is negative. This condition implies a high equilibrium yield for the reaction as written in equation (6) at sufficiently high reactor temperatures.

The results of the experiments are presented in Table 6. Generally, the results show that for the temperature range under study, silicon will be etched from the bed when the ratio of hydrogen to tetrabromosilane is not maintained above about 7 to 1. A substantial quantity of tribromosilane was collected in the low-temperature condensers downstream from the reactor outlet. In additions, HBr was isolated and identified by its boiling point. A slight amount of wall deposition was noted within the reactor; however, when compared with the amount of silicon etched from the fluidized bed, the deposits were materially insignificant. These observations and the detailed results presented in Table 6 lead to the conclusion that the following partial reduction reaction was occurring.



The free energy change for this reaction can be calculated by previously illustrated methods. This shows that $G = -8.18 \text{ Kcal/mol}$ at 25°C, and, therefore, is thermodynamically favorable. The results of these hydrogen reduction experiments, presented in Table 6, enable one to infer that reaction (1) proceeds more readily than reaction (6), since under the same experimental conditions there was a net loss of elemental silicon in two of three tests.

*see Appendix

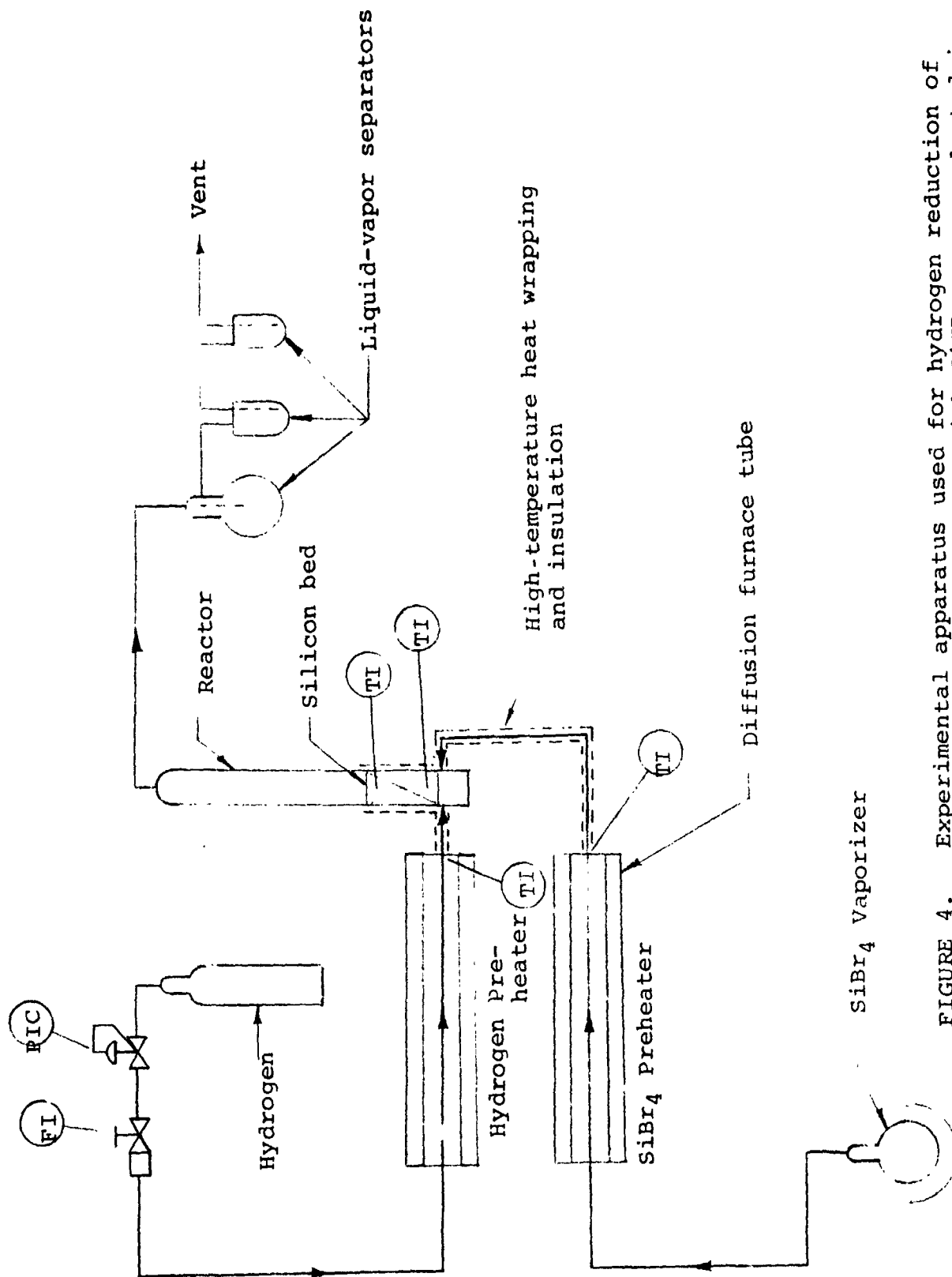


FIGURE 4. Experimental apparatus used for hydrogen reduction of SiBr₄. Initial experiment with SiHBr₃ was conducted in this apparatus with the result of very heavy wall deposits at inlet and exit of SiBr₄ Preheater.

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TABLE 6

RESULTS OF HYDROGEN REDUCTION OF TETRABROMOSILANE IN A FLUIDIZED BED REACTOR

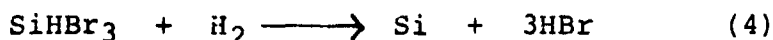
RUN I.D.	T _r °C	H ₂ :SiBr ₄ Ratio	Δ Si BED %	REMARKS
A	1000	5.5	-25.0%	Considerable SiHBr ₃ in condensed effluent. Slight wall deposits.
B	1050	5.9	-2.5%	Charge consisted of Si rock. Most of surface was etched. Small area having deposition noted. Liquid effluent contained SiHBr ₃ .
C	1000	12.0	+0.9%	Effluent was recycled. Increase in Si may be due to SiHBr ₃ in effluent recycled. About 1/2 of surfaces showed etching. Final liquid effluent contained SiHBr ₃ .

Note: Test runs A, B, and C were each conducted for 240 minutes.

4.4 Decomposition of SiHBr₃ in a Fluidized Bed Reactor

4.4.1 General

The goal of these experiments was to determine the rate of silicon production and the influence of such variables as reactor temperature, feed rate of reactants, residence time, and the ratios of hydrogen to tribromosilane. The anticipated reduction reaction,



was expected to be thermodynamically favorable at elevated temperature, since

$$\Delta G = 0 \text{ Kcal/mol at } 1234^\circ\text{C}$$

The fact that this reaction was found to proceed at lower temperatures suggests possible errors in the thermodynamic data available in the literature (13), (14)*

The initial fluidized bed experiment utilizing tribromosilane as the silicon precursor was conducted in the same experimental apparatus as used for the work with tetrabromosilane (Figure 4).

The results of the initial experiment indicated a high degree of decomposition even without the presence of hydrogen. This result led to a series of thermal stability tests and subsequently to a series of fluidized bed thermal decomposition and hydrogen reduction experiments.

4.4.2 Thermal Stability of Tribromosilane

The initial fluidized bed experiment was terminated prematurely due to a rupture in the tribromosilane preheater. The ruptured heater line was found to have heavy wall deposits in the low temperature regions at both the inlet and exit. This unexpected result precipitated a thermal stability study before additional fluid bed experiments were undertaken. The study was undertaken to determine in what temperature realms significant decomposition occurs and to determine the influence of the presence of hydrogen. An experimental decomposition chamber having five independently controlled temperature regions was constructed. This apparatus is depicted in Figure 5. For experiments without hydrogen, the tribromosilane was metered as liquid to the flash vaporizer. When hydrogen was

*see Appendix

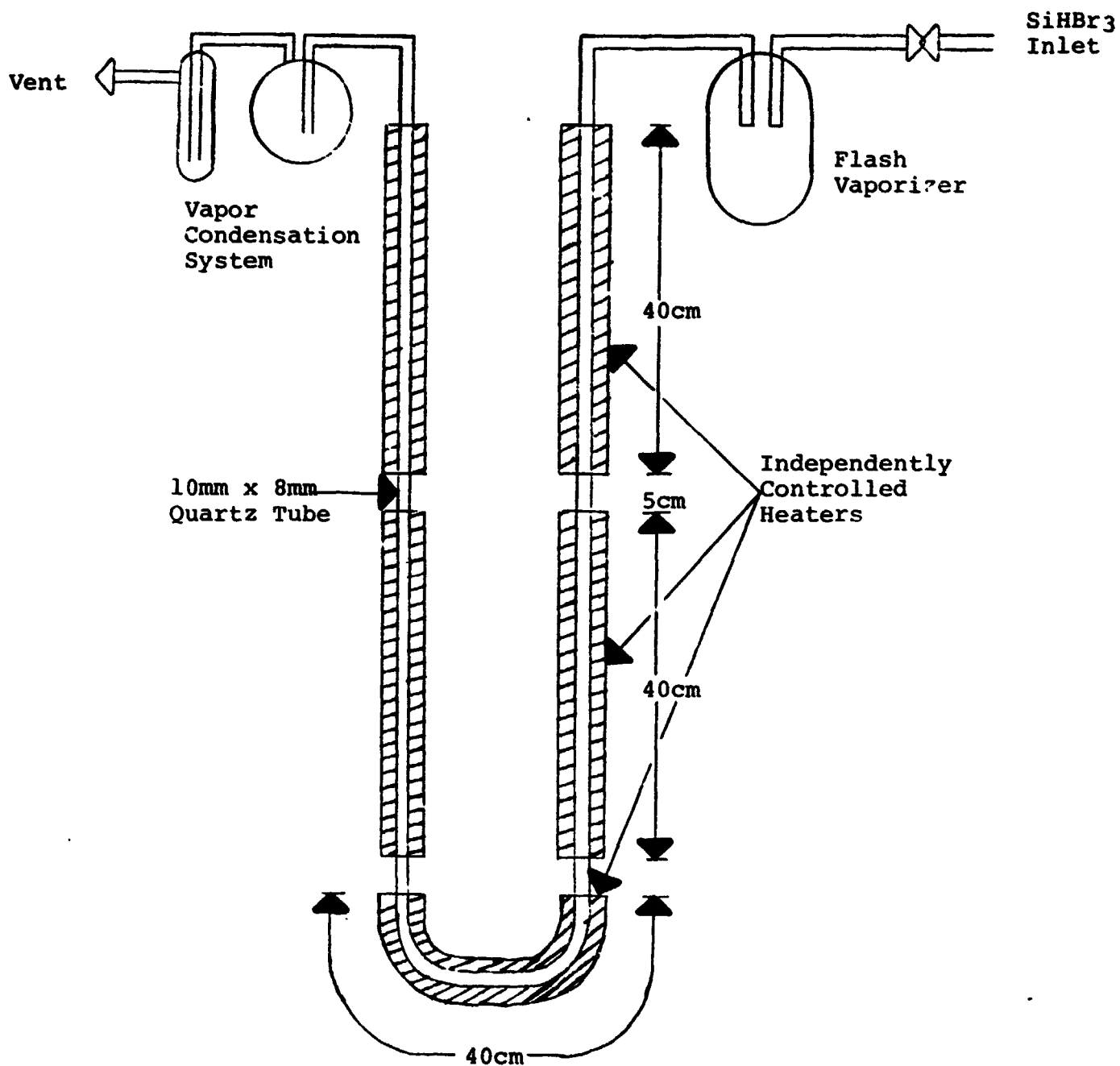


FIGURE 5

THERMAL DECOMPOSITION TEST CHAMBER
AND APPARATUS USED IN THE THERMAL
STABILITY INVESTIGATIONS OF
TRIBROMOSILANE.

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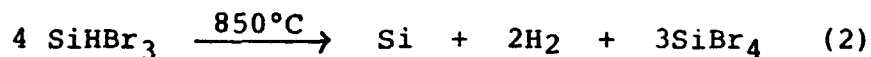
used, it was bubbled through a thermostated flask of tribromosilane. The flask temperature was regulated to give the desired molar ratio of hydrogen. The results are given in Table 7. The most significant observations are that occurred.

- (a) Without hydrogen, silicon is deposited at a substantial rate in the temperature range of 550°C - 900°C
- (b) Without hydrogen, silicon is not deposited at temperatures above 900°C
- (c) Hydrogen resulted in an upward shift in the temperature at which deposits of silicon occurred.
- (d) No silicon base polymer was detected

4.4.3. Fluidized Bed Reactor Experiments

Following the thermal stability experiments, the fluidized bed reactor was modified by eliminating the feed preheaters and a series of experiments was undertaken to exploit the relatively low temperature thermal decomposition of tribromosilane. A schematic diagram showing the revised experimental apparatus is given in Figure 6.

Thermodynamically, the decomposition reaction



can be shown to be favorable. That is,

$$\Delta G = \Delta H - T\Delta S = 8.5 \text{ Kcal/mole @ } T = 25^\circ\text{C} *$$

The initial series of experiments, numbers 001 through 009, was conducted with the following goals:

- (a) Determine the quantitative yield of silicon as a function of residence time.
- (b) Determine the influence of residence time and feed rate of tribromosilane on silicon yield.

*see Appendix

TABLE 7

RESULTS OF THERMAL DECOMPOSITION
STUDIES OF TRIBROMOSILANE

Temp. K ^o	Ratio H ₂ :SiHBr ₃	Observations and Results
700-800	N/A	Very slight deposits having appearance of metallic foil.
940-1000	N/A	Opaque, black silicon deposit
1075-1100	N/A	Heavy, opaque, black silicon deposits
1325	N/A	No silicon deposit
1075	N/A	Isothermal experiment. Heavy, black deposits at boundary to hot zone. Slight translucent metallic foil like deposit throughout hot zone.
Up to 1175	22	No silicon deposit
1175-1275	22	Very heavy deposit. About 1 mm thick
Above 1275	22	No silicon deposit

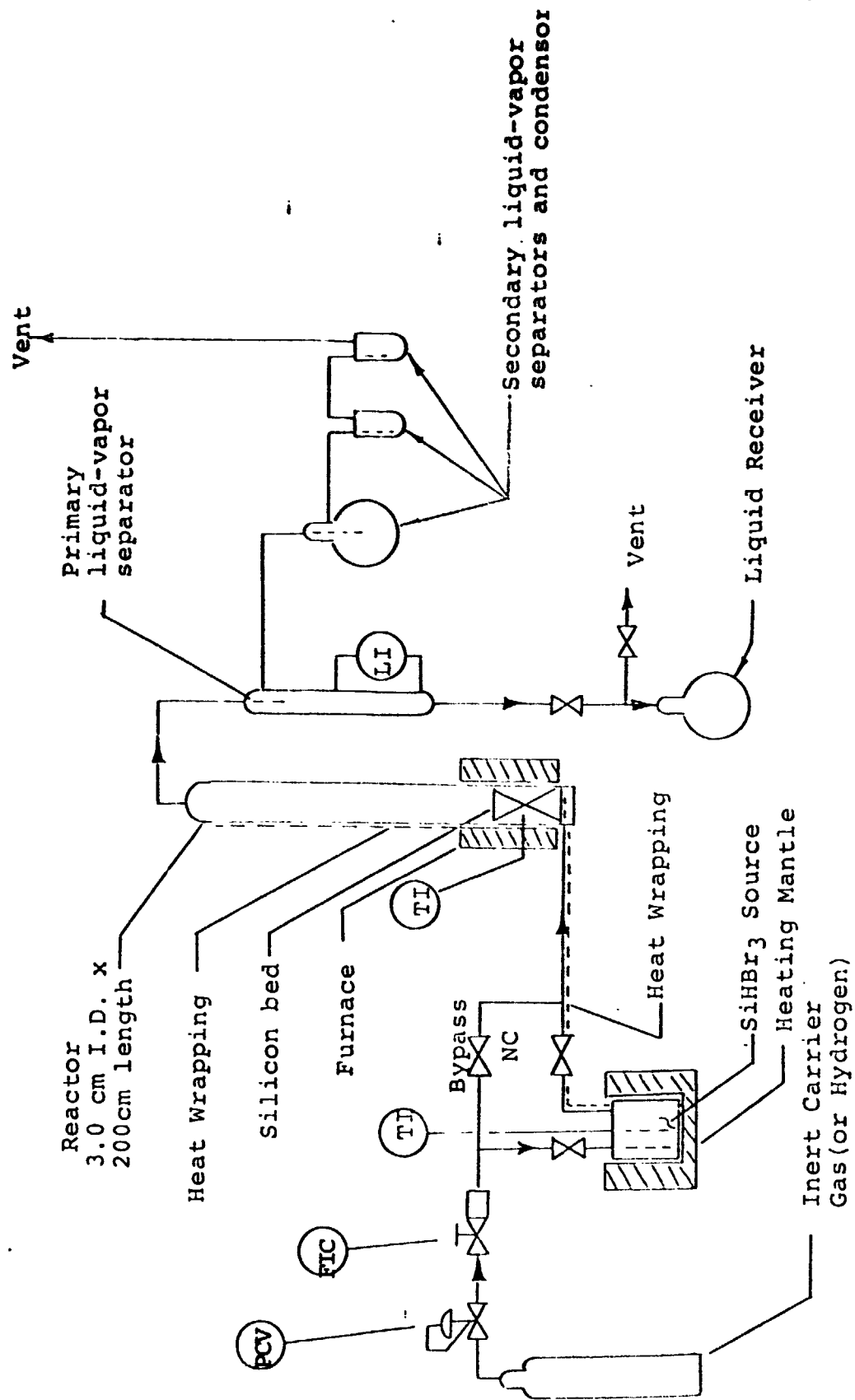


FIGURE 6

Experimental apparatus used for thermal decomposition of tribromosilane in the fluidized bed reactor. This same apparatus was used for the hydrogen reduction experiments.

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The experimental method consisted of feeding a measured quantity of tribromosilane per unit of time into a fluidized bed having a known mass of silicon substrate particles. The condensible effluent gasses were collected. The carrier gas and non-condensable effluents were vented. The silicon yield was determined gravimetrically by measuring the change in the silicon bed and relating it to the theoretical yield indicated by equation (24).

A sample yield calculation is illustrated for experiment 006.

$$\begin{aligned}
 \% Y &= \frac{\text{g Si} \times 100\%}{\text{Gr} \frac{(273)}{(273+850)} \left(405 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \right) \left(\frac{\text{g mol}}{22400 \text{ cm}^3} \right) (28 \text{ g Si}) (0.25)} \quad (24) \\
 &= \frac{9.20 \text{ g Si} \times 100\%}{\left(\frac{6.9 \text{ cm}^3}{\text{s}} \right) (0.243) (24300 \text{ s}) \left(\frac{28 \text{ g Si}}{22400 \text{ cm}^3} \right) (0.25)} \\
 &= \frac{920}{12.73} \% \\
 &= 72.3\%
 \end{aligned}$$

A second series of experiments, numbers 010 through 019, was conducted with yield determinations being made by chromatographic analysis of the reactor effluent. That is, a reactor effluent found to contain 25% tribromosilane was interpreted to imply a 75% decomposition and hence a yield equivalent to 75% of the theoretical.

This correlation of reactor effluent composition to the gravimetric yield of silicon for a particular set of reaction parameters was demonstrated to be correct in Experiment 020. The results of this experiment show a deviation of about 4% between yield data determined by the two methods, the high value being determined by chromatography. A sample chromatogram is given in Figure 7, and the summary of the experimental data and results for Experiments 001 through 020 are given in Table 8.

4.4.4. SiHBr₃ Thermal Decomposition Product Silicon Appearance and Size Analysis

Silicon, charged to and removed from the fluidized bed reactor, was analyzed by ASTM standard sieves to determine the average changes in particle size and changes in particle size distribution. The results of a typical sieve analysis is shown graphically in Figure 8. Because of the small particle size, generally less than 350μ diameter, unaided visual inspection is inadequate. Photomicrographs of product silicon at several magnifications show that the angularity of the product is main-

DATA:

Sample: 11-13-1, Reactor Effluent, Experiment 202
Size: 2.0 microliters
Solvent: none

Column Temperature & Program:

Initial: 60°C for 3 min.
Rate: 10°/min.
Final: 290°C for 3 min.

Column: 400 cm, glass
Packing: 10% OV-101
Carrier: Helium @ 20 cm³/min
Thermal Conductivity Detector

SiHBr₃
A = 675 mm²
% = 54.3

Retention = 8.1 min

SiBr₄
A = 567 mm²
% = 45.7

Retention = 11.5 min

Sample Injection

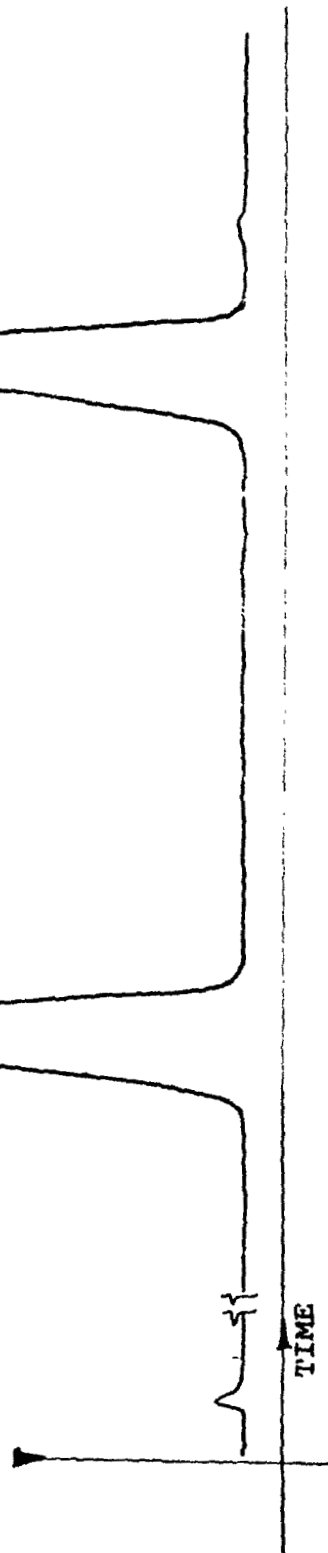


FIGURE 7. Typical chromatogram showing tribromosilane and tetrabromosilane peaks. This illustrates the reactor effluent analysis for Experiment 202, Table 9 .

RESULTS OF THERMAL DECOMPOSITION EXPERIMENTS OF TRIBROMOSILANE IN

I. D.	DATE	REACTOR DATA			CARRIER GAS	SiHBr ₃	U _o
		d _r cm	L _f cm	T _r	G _c (I) cm ³ /s	G _r (I) cm ³ /s	cm/s
001	19 July 1978	3.0	35.0	750	57.2	6.5	9.0
002	20 July	3.0	35.0	825	61.4	9.8	10.2
003	24 July	3.0	26.0	775	58.6	4.6	9.0
004	26 July	3.0	26.0	725	55.8	8.9	9.2
005	27 July	3.0	26.0	800	90.0	18.5	15.5
006	31 July	3.0	25.0	850	62.8	6.9	10.0
007	02 August	3.0	21.0	900	65.6	5.8	10.2
008	03 August	3.0	13.0	750	85.8	22.0	15.4
009	04 August	3.0	13.0	750	42.9	52.1	13.6
010	21 Sept.	3.0	5.4	550	91.1	33.9	17.5
011	21 Sept.	3.0	5.4	632	101.2	37.3	19.1
012	23 Sept.	3.0	5.4	650	103.2	38.0	19.6
013	23 Sept.	3.0	5.4	710	109.9	40.5	20.7
014	23 Sept.	3.0	5.4	752	114.7	42.2	21.7
015	23 Sept.	3.0	5.4	800	120.0	44.2	22.7
016	23 Sept.	3.0	5.4	854	126.1	46.4	23.9
017	23 Sept.	3.0	5.4	945	136.2	50.1	26.0
018	26 Sept.	3.0	5.4	675	106.0	39.0	20.1
019	26 Sept.	3.0	5.4	700	108.8	40.1	20.7
020	24 Oct.	3.0	15.0	805	72.4	18.5	12.9

NOTES:

- (1) G_c and G_r are calculated on the basis of T_r.
 (2) Determined chromatographically.

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TABLE 8

EXPERIMENTAL DATA OF TRIBROMOSILANE IN A FLUIDIZED BED REACTOR

TRIAL NO.	SiHBr ₃ Gr (l) cm ³ /s	U ₀ cm/s	T _r s	YIELD g, Si	RUN TIME Min.	YIELD %
.2	6.5	9.0	3.9	1.00	325	9.4
.4	9.8	10.2	3.4	13.89	255	118.7
.6	4.6	9.0	2.9	6.43	400	71.2
.8	8.9	9.2	2.8	7.65	240	70.1
.0	18.5	15.5	1.7	13.27	240	62.5
.8	6.9	10.0	2.5	9.20	405	72.3
.6	5.8	10.2	2.1	2.16	240	35.5
.8	22.0	15.4	0.8	4.91	120	37.1
.9	52.1	13.6	1.0	21.96	220	38.3
.1	33.9	17.5	.31	N/A	N/A	2.2 (2)
.2	37.3	19.1	.28	N/A	N/A	14.3 (2)
.2	38.0	19.6	.27	N/A	N/A	17.8 (2)
.9	40.5	20.7	.26	N/A	N/A	59.3 (2)
.7	42.2	21.7	.25	N/A	N/A	60.6 (2)
.0	44.2	22.7	.24	N/A	N/A	83.2 (2)
.1	46.4	23.9	.22	N/A	N/A	87.0 (2)
.2	50.1	26.0	.20	N/A	N/A	89.4 (2)
.0	39.0	20.1	.27	N/A	N/A	20.2 (2)
.8	40.1	20.7	.26	N/A	N/A	41.6 (2)
.4	18.5	12.9	1.16	25.34	420	80.5
						84.7 (2)

basis of T_r.ORIGINAL PAGE IS
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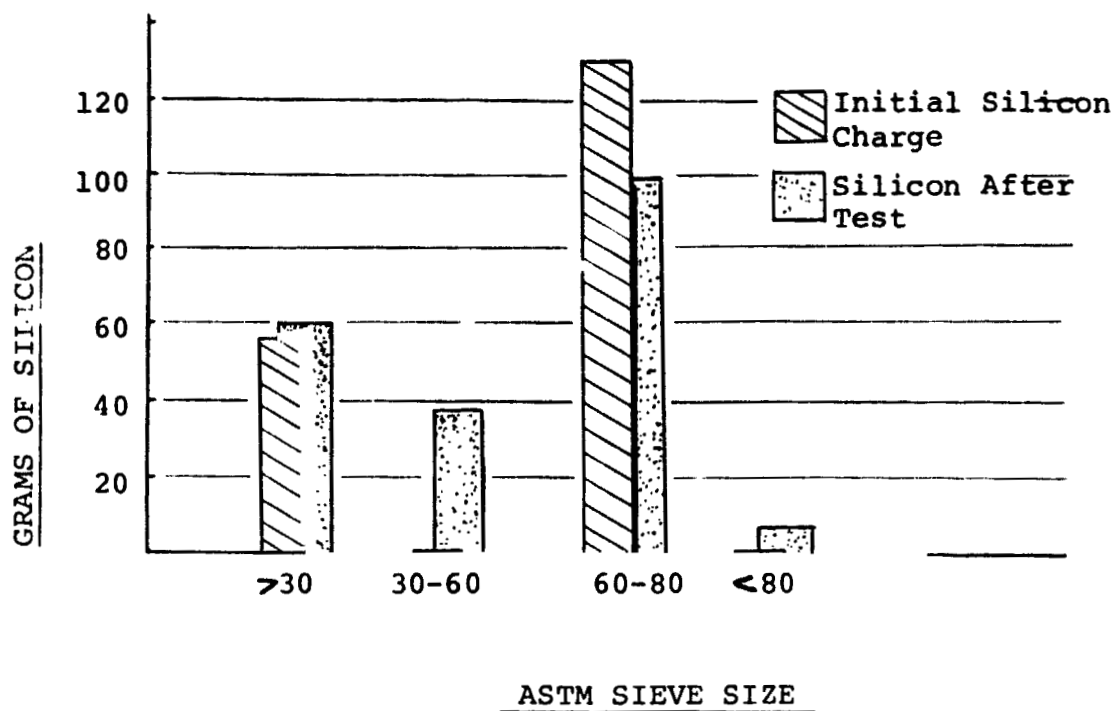


FIGURE 8. Typical sieve sizing analysis showing shift toward larger silicon particles and change in distribution of particles. Results shown are for tribromosilane thermal decomposition in the fluidized bed reactor.

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Figure 9. Silicon seed particles at 100 x. Note nodular silicon deposition on surfaces.



Figure 10. View of area marked in Figure 9. This view at 2000 x shows denseness of deposition.

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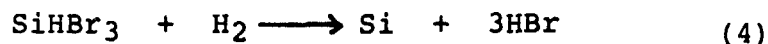


Figure 11. 5000 x view of same silicon product as shown in Figures 9 and 10. No porosity or voids are evident.

tained through the processing and that the silicon deposited has a dense, nodular appearance. Figures 9, 10 and 11 illustrate these observations.

4.5. Hydrogen Reduction of Tribromosilane in a Fluidized Bed Reactor

Two experiments utilizing hydrogen as a reducing agent were conducted in the fluidized bed reactor apparatus illustrated in Figure 6. These experiments were designed to capitalize on the more favorable yields of silicon as indicated by Equation (4), e.g.,



in comparison to the thermal decomposition yield [Equation (2)]. In the latter case, for each four moles of silicon input to the reactor, a maximum of one mole of silicon can be deposited as product, whereas the hydrogen reduction reaction has a mole for mole correspondence.

The results of these experiments showed silicon yields of 35% and 60% of theoretical at the temperatures investigated. In these experiments, the silicon yield was determined gravimetrically. The condensable effluents were found to contain substantial amounts of non-reduced tribromosilane as well as tetrabromosilane. The experimental data are presented in Table 9.

4.6 Conversion of Tetrabromosilane to Tribromosilane

4.6.1. General

The favorable reaction yields from the thermal decomposition reaction (2)



and from the hydrogen reduction reaction (4)



suggest the possibility of economically viable processes capable of meeting the LSA cost goals for 1986. The previous attempts to reduce tetrabromosilane with hydrogen in the fluidized bed reactor resulted in the erosion of the silicon bed and the production of tribromosilane. This observation, coupled with the

TABLE 9

RESULTS OF HYDROGEN REDUCTION OF TRIBROMOSILANE IN A FLUIDIZED BED REACTOR

I.D. NUMBER	DATE	REACTOR DATA			HYDROGEN		SiHBr ₃		U ₀		Yield	YIELD(2)	SiHBr ₃ (3)
		d _r cm	L _f cm	T _r °C	G _G cm ³ /s(1)	G _r cm ³ /s(1)			cm/s	s	g, Si	%	%
201	2 Nov.	3.0	14.2	950	112.0	7.3			16.9	0.84	21.3	35.2	36.3
202	7 Nov.	3.0	14.2	1000	116.6	7.6			17.6	0.81	28.9	58.9	25.2

NOTES:

- (1) Relative to T_r
- (2) Expressed as a percent of maximum theoretical.
- (3) Mole percent of tribromosilane in condensibles from reactor.

favorable silicon yield data, indicated the possibility of two closed loop processes for the production of solar grade silicon. The ultimate success of either process required the conversion of by-product tetrabromosilane into tribromosilane at some suitably high yield. A series of experiments directed toward this needed conversion was undertaken.

4.6.2 Packed Bed Experiments

A series of three experiments was undertaken in the apparatus shown in Figure 12 to investigate the temperature dependence of the yield of tribromosilane via Equation (1). The reactor was packed with lumps of metallurgical grade silicon, and strands of copper wire were dispersed throughout the bed to act as a reaction catalyst. Pure tetrabromosilane synthesized from bromine and silicon was introduced along with hydrogen into the reactor. The reactor effluent was condensed and distilled into products by noting boiling point. A plot of volume collected vs. boiling point was made and used to compute the yield of tribromosilane. A sample volume vs. boiling point diagram is shown in Figure 13.

4.6.3 Fluidized Bed Experiments

Six additional experiments were conducted using a fluidized bed reactor. Experiments 104 through 106 employed 3 wt % copper powder as catalyst, while the final three Experiments 107 through 109 were conducted without the benefit of a catalyst.

The experimental data and results for runs 101 through 109 are summarized in Table 10. Review of these data indicate commercially acceptable yields of tribromosilane and show that

- (a) Yield of tribromosilane is greatest in a temperature range of 650°C to 700°C.
- (b) Yield is improved by increasing residence time.
- (c) Hydrogen to tetrabromosilane ratios of 1:1 to 2.5:1 resulted in highest yields.

The importance of a reaction catalyst and the value of a fluidized bed for the conversion reaction were not conclusively demonstrated in the experiments.

The 35% yield of tribromosilane, coupled with the silicon yields of the thermal decomposition and hydrogen reduction processes, indicates two possible closed-loop processes as potential ones for commercialization.

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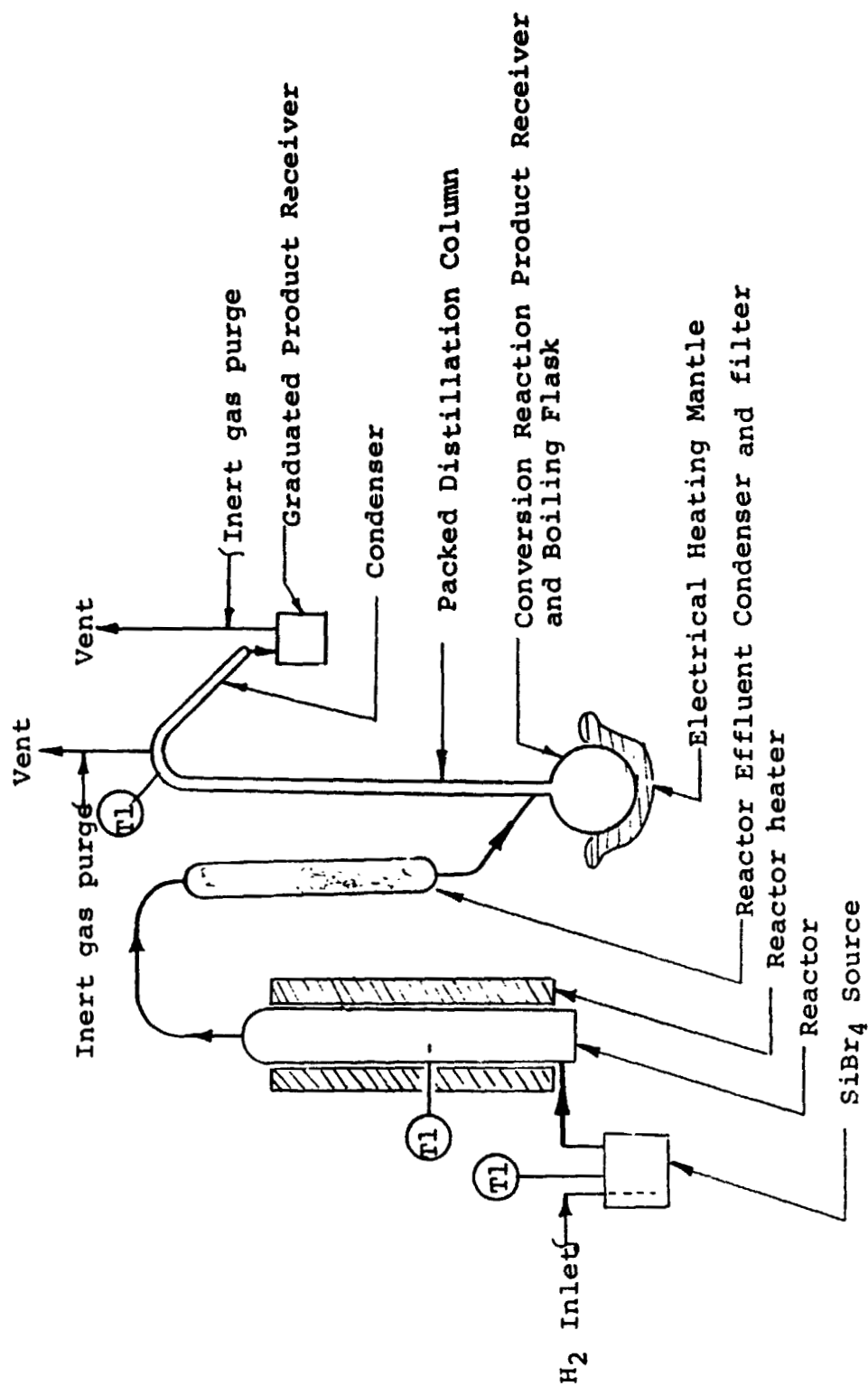


FIGURE 12: Experimental apparatus for conversion of tetrabromosilane to tribromosilane. Refer to Table 10 for experimental data.

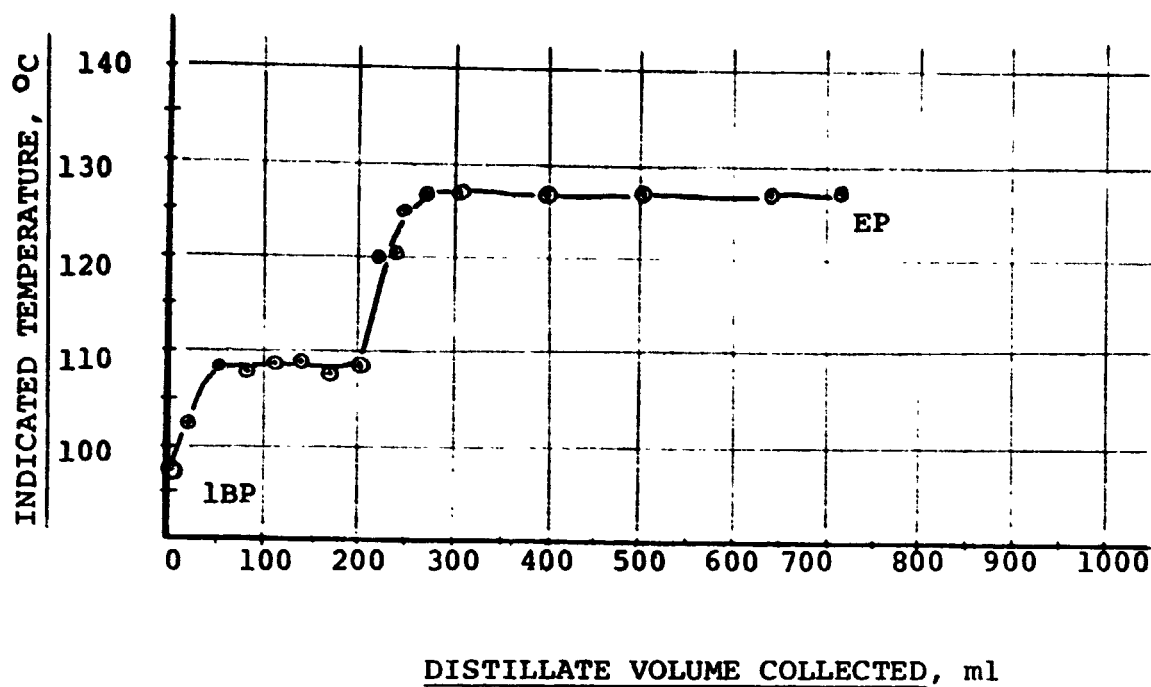


FIGURE 13. Typical plot showing volume vs. boiling point for analysis of conversion reaction. Results show approximately 200 ml SiHBr_3 in a total volume of 710 ml. Refer to Table 10 , Experiment 102 for details.

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TABLE 10

RESULTS OF CONVERSION OF TETRABROMOSILANE TO TRIBROMOSILANE

NUMBER	DATE	REACTOR DATA			HYDROGEN		SiBr ₄		RATIO		U ₀ cm/s	s	YIELD SiHBr ₃ % (2)	CATALYST	REMARKS
		dr cm	Ls cm	Tr °C	G _c (1) cm ³ /s	G _c (1) cm ³ /s	G _r (1) cm ³ /s	G _c / G _r							
101	1-6 June	2.4	40	620	25.0	14.3	1.75	8.7	4.6	21	Strands of copper wire	Packed bed			
102	13 June	2.4	40	650	26.1	11.7	2.23	8.3	5.1	36					
103	15-16 June	2.4	40	698	27.2	33.9	0.80	13.5	3.0	37					
104	28 June	2.5	20	560	46.6	8.8	5.30	11.3	1.8	Nil	No catalyst	Fluidized bed			
105	5 July	2.5	20	600	24.4	30.1	0.81	11.1	1.8	8					
106	7 July	2.5	20	675	42.4	18.0	2.35	12.3	1.6	13					
107	11 July	2.4	10	650	14.8	34.4	0.43	10.8	0.9	12	Copper powder	Fluidized bed			
108	12 July	2.4	10	690	8.1	14.7	0.55	5.0	2.0	15					
109	12 July	2.4	10	550	46.0	14.9	3.09	13.5	0.7	Nil					

NOTE:

(1) Relative to Tr

(2) Yield is defined as the ratio of moles of SiHBr₃ to moles of SiBr₄ x 100%

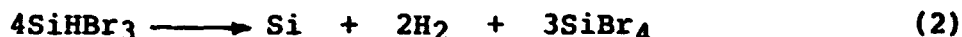
5.0 CLOSED-LOOP PROCESS FOR SOLAR GRADE SILICON PRODUCTION FROM SiHBr_3

5.1 General

The experimental investigations reported in Sections 3.0 and 4.0 substantiate the design of two closed-loop processes for the production of silicon. These processes rely upon the decomposition of tribromosilane or the hydrogen reduction of tribromosilane in a fluidized bed reactor and the subsequent production of fresh tribromosilane by the reaction of reactor by-products with hydrogen and metallurgical grade silicon. These processes are described in detail in the following paragraphs.

5.2 Thermal Decomposition Process

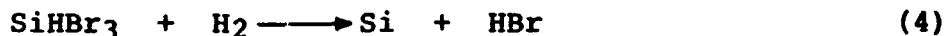
This process utilizes the observed thermal decomposition reaction of tribromosilane,



coupled with the conversion of the tetrabromosilane by-product to fresh tribromosilane. A block flow diagram of this process is given in Figure 14. A simplified process flow diagram and material balance is given in Figure 15.

5.3 Hydrogen Reduction Process

The hydrogen reduction of tribromosilane,



is the basis for this process. The generation of fresh tribromosilane is accomplished by the conversion of by-product tetrabromosilane and the production of additional material from the reaction of HBr and Si as reported by Schumb & Young (15). A block flow diagram is shown in Figure 16 and a simplified process flow diagram and material balance in Figure 17.

5.4 Process Economics

Since each closed-loop process shows great promise and has demonstrated technical feasibility, the process selection requires evaluation of the economic parameters of each process. A simplified economic analysis is presented in Table 11 for the two competing processes.

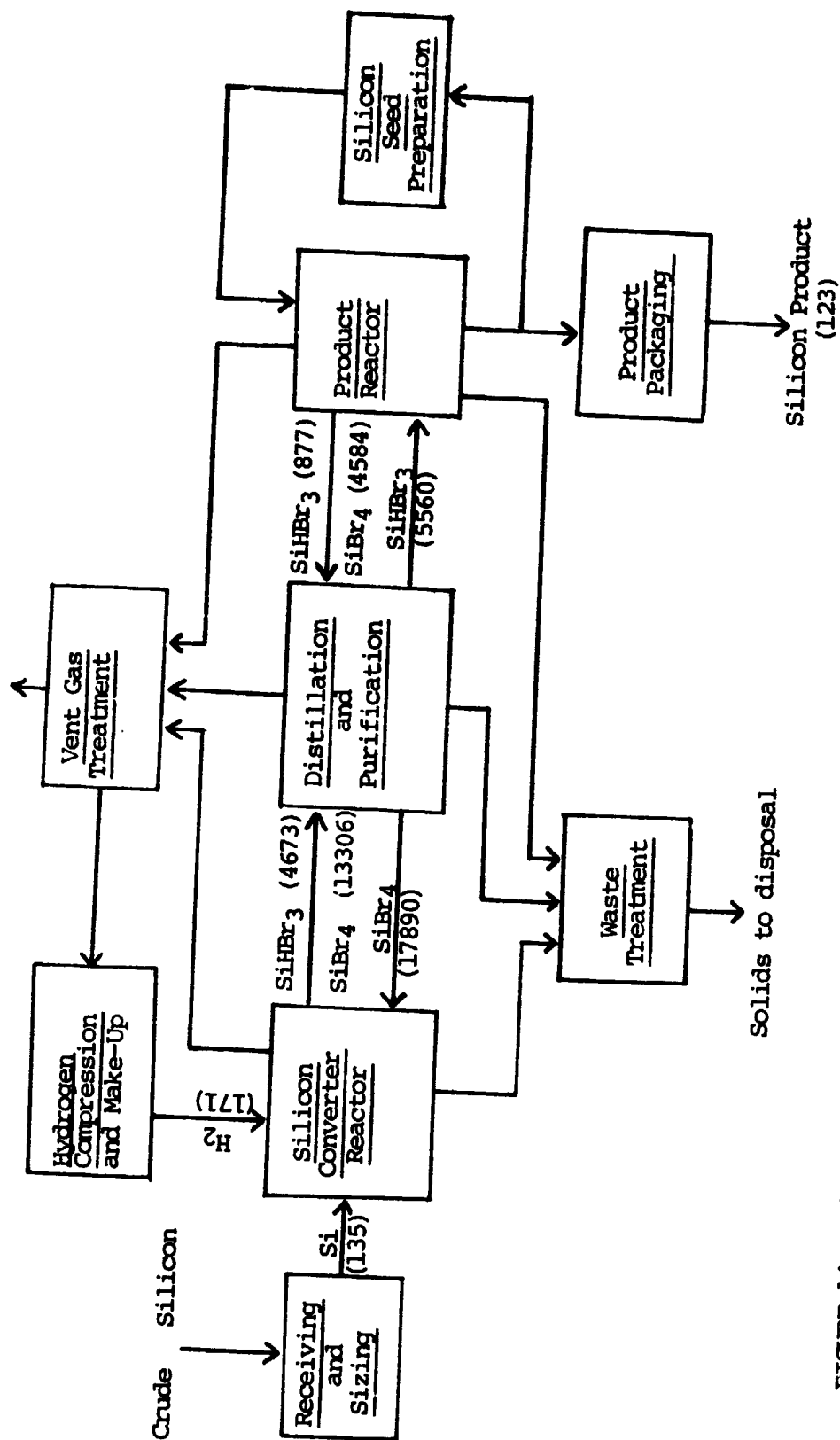
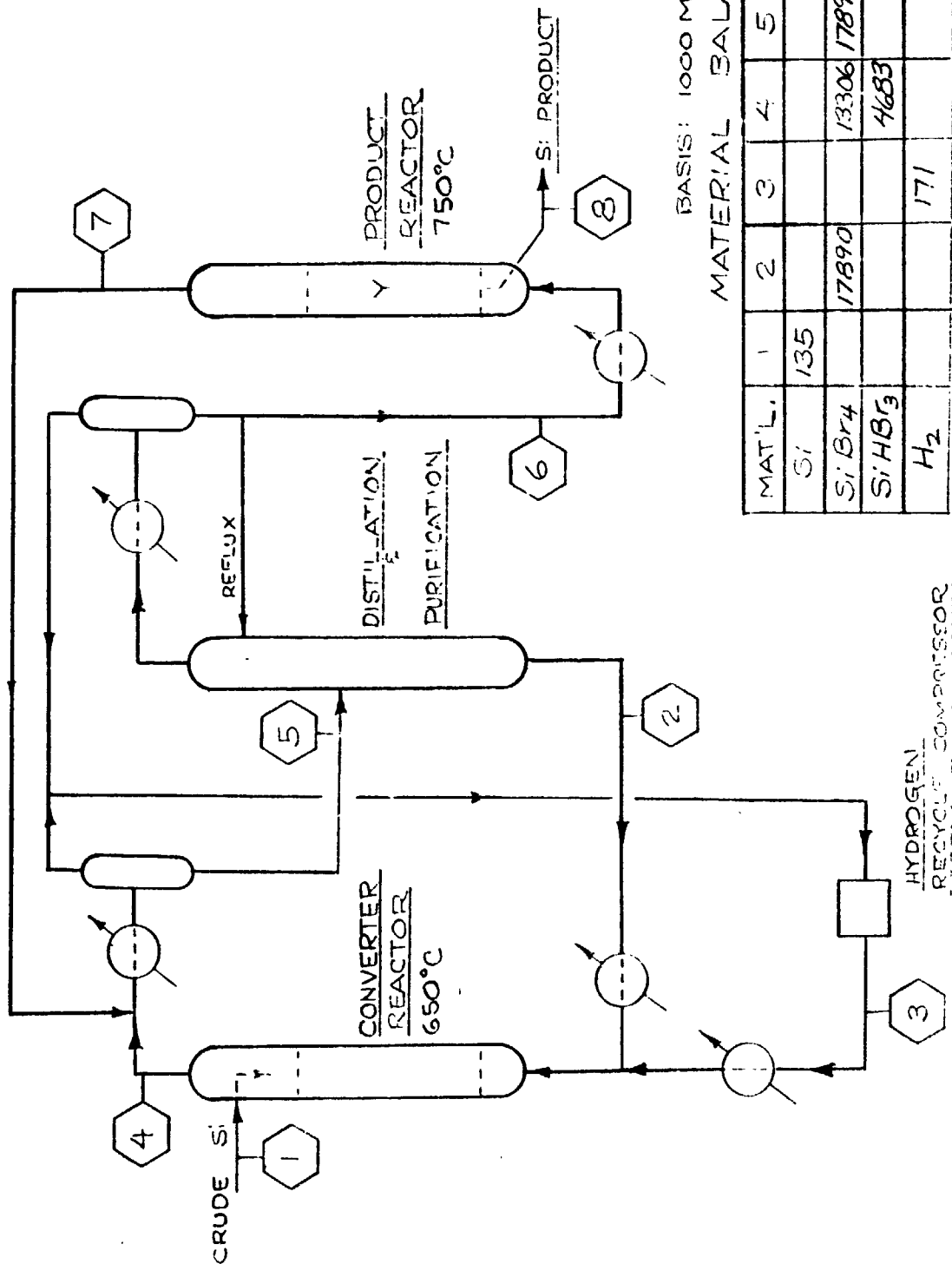


FIGURE 14. Simplified block flow diagram showing Closed-Loop Thermal Decomposition Process. Flow rates in kg/h are shown for major streams for a 1000 MT/Y plant.

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BASIS: 1000 MT/Y
MATERIAL BALANCE kg/h

MAT'L.	1	2	3	4	5	6	7	8
Si	135							123
SiBr ₄		17890		13306	17890		4584	
SiHBr ₃				4683		5560	877	
H ₂			171					

FIGURE 15. SIMPLIFIED PROCESS FLOW DIAGRAM & MATERIAL BALANCE - THERMAL DECOMPOSITION PROCESS

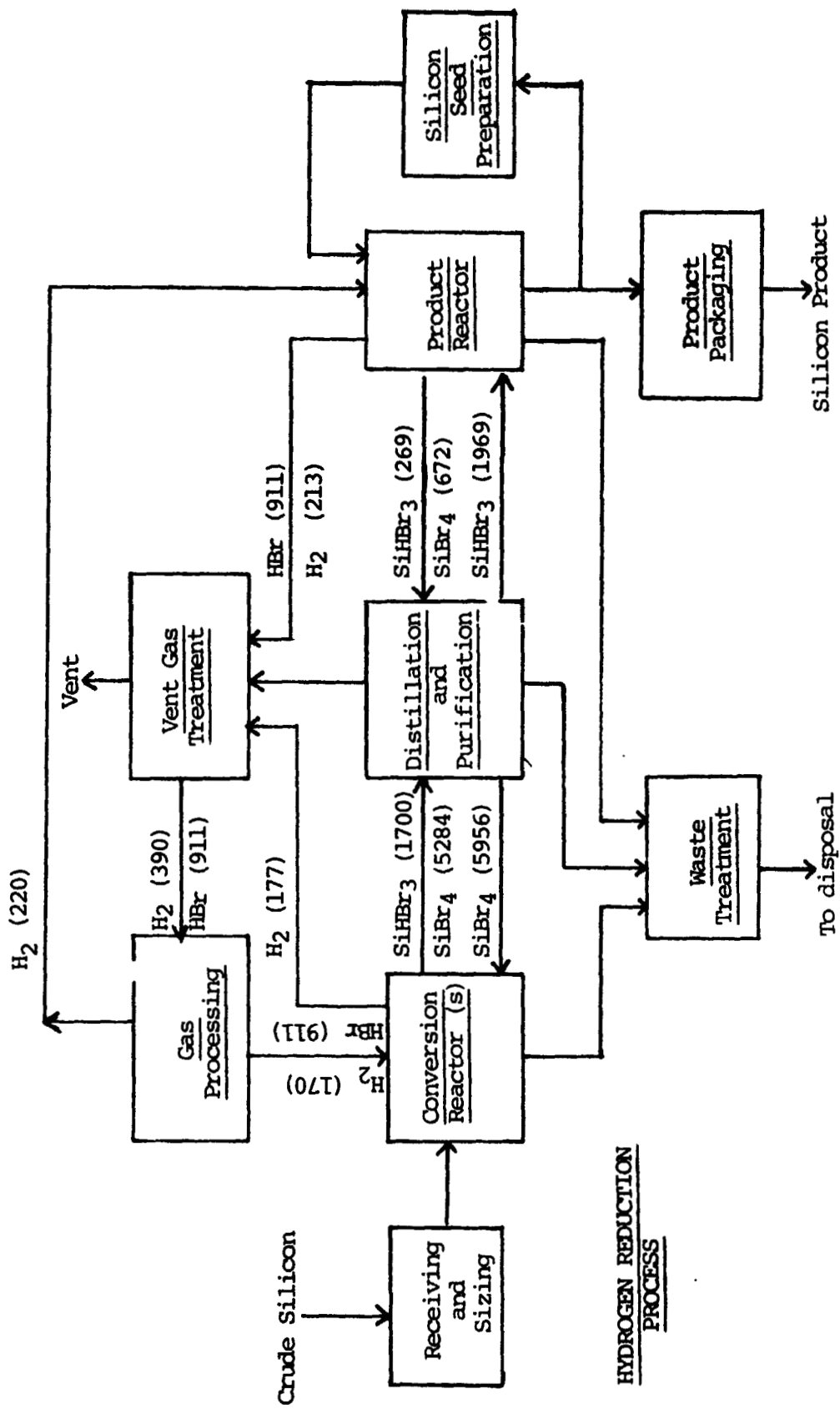


FIGURE 16. Simplified block flow diagram for Hydrogen Reduction Process.
Major process streams show flow rates in Kg/h for 1000 MT/Y plant.

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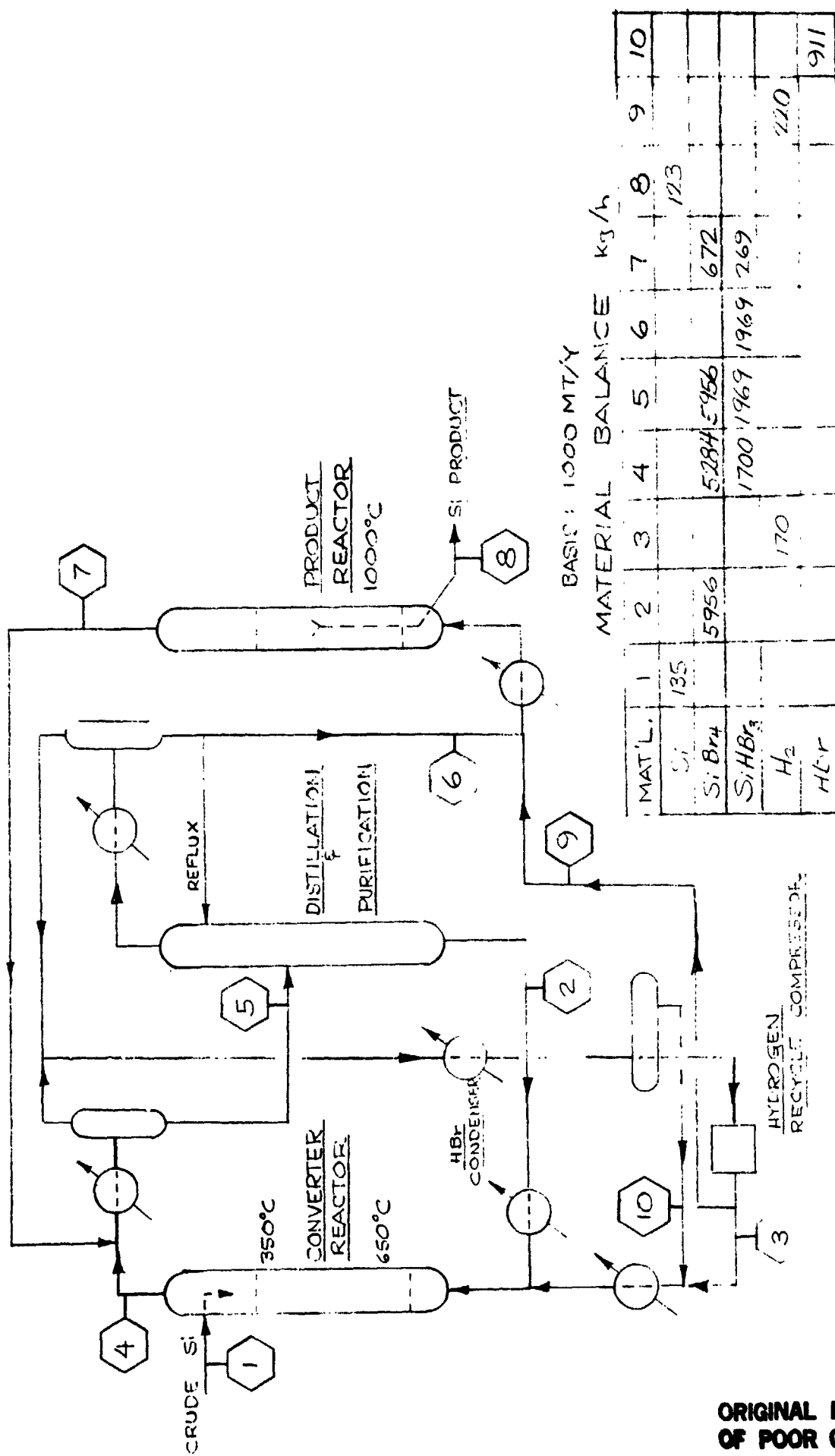


FIGURE 17. SIMPLIFIED PROCESS FLOW DIAGRAM & MATERIAL BALANCE
HYDROGEN REDUCTION PROCESS

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Cost estimates presented in Table 11 show that neither process has a clear economic advantage in terms of Capital Costs. The processes are technically similar and have comparable energy requirements; hence, operating costs may be reasonably expected to be about equal.

5 Process Selection

The Thermal Decomposition and Hydrogen Reduction Processes are technically similar. Major points for comparison of the two processes are:

Thermal Decomposition Process

- (1) larger process units with higher throughput
- (2) simpler process due to lack of HBr reactions
- (3) lower reaction temperatures
- (4) 30% overall theoretical yield demonstrated

Hydrogen Reduction Process

- (1) process units 1/3 size of thermal decomposition process with corresponding lower through-put
- (2) more complicated process due to HBr reactions
- (3) higher reaction temperatures
- (4) 36% overall theoretical yield demonstrated

However, it must be recognized that although each process has three basic process steps (with one of these, the purification stage, common to both processes), only one non-common stage in each process has been extensively studied, and to a certain degree optimized. These are the decomposition (last) stage in the Thermal Decomposition Process and the synthesis (first) stage in the Hydrogen Reduction Process, the latter being utilized for SiHBr_3 synthesis prior to and during the life of the contract.

At this point then, both processes appear attractive as well as comparable; and further optimization of SiHBr_3 synthesis from SiBr_4 and H_2 , as well as hydrogen reduction of SiHBr_3 , to determine maximum overall process yield and reaction rate are required for process selection.

TABLE 11

Order of magnitude estimates of capital costs associated with construction of 1000 MT/Y silicon production plant. The Thermal Decomposition Process and the Hydrogen Reduction Processes are compared.

<u>CAPITAL COSTS (1)</u>	<u>H₂ REDUCTION (2)</u>	<u>THERMAL DECOMPOSITION</u>
Direct Costs		
Process Equipment	\$ 3,600,000	\$ 4,365,000
Process Material	1,700,000	1,690,000
Piping	1,400,000	1,435,000
Electrical	325,000	300,000
Insulation	652,000	652,000
Structural	1,300,000	1,300,000
Instrumentation	430,000	430,000
Offsites	1,500,000	1,500,000
Labor	1,430,000	1,440,000
Total Direct Costs	<u>12,337,000</u>	<u>13,242,000</u>
Indirect Costs		
Contractors Expenses & Fee @ 15%	1,850,550	1,986,300
Total Indirect Costs	<u>1,850,550</u>	<u>1,986,300</u>
Total Installed Cost	<u>\$14,187,550</u>	<u>\$ 15,228,600</u>

Notes:

- (1) Total direct and indirect costs scaled from process equipment element estimates using typical cost factors from Perry. (16)
- (2) Cost estimate derived from process equipment estimate for thermal decomposition process through use of "six-tenths factor" in Perry.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Based on the studies described above the following conclusions can be drawn.

- 1) Technical feasibility of two closed-loop SiHBr_3 processes, the Thermal Decomposition and the Hydrogen Reduction Process, for production of SCG polycrystalline silicon, has been demonstrated by laboratory-scale experiments.
- 2) SiHBr_3 processes studied possess certain technical and economic advantages over current SG polycrystalline production and chlorosilane based processes for meeting LSA Project Silicon Material Task cost objectives. These are:
 - i) Continuous rather than batch operation of the reduction stage.
 - ii) Reduced energy consumption per unit of Si product through continuous reduction at reduced temperature.
 - iii) Inhibited homogeneous nucleation and wall deposition.
 - iv) Elimination of formation of explosive polymer products.
 - v) Large-particle (350 micron) product.
- 3) Comparative simple economic analysis shows the Thermal Decomposition Process and the Hydrogen Reduction process both have Capital Equipment Cost Estimates in the range of the Cost Element Objective of \$15,000,000 for 1,000,000 kg/yr polycrystalline silicon production.
- 4) Further study will be required for process selection and completion of raw material, utility, and operating labor cost estimates.

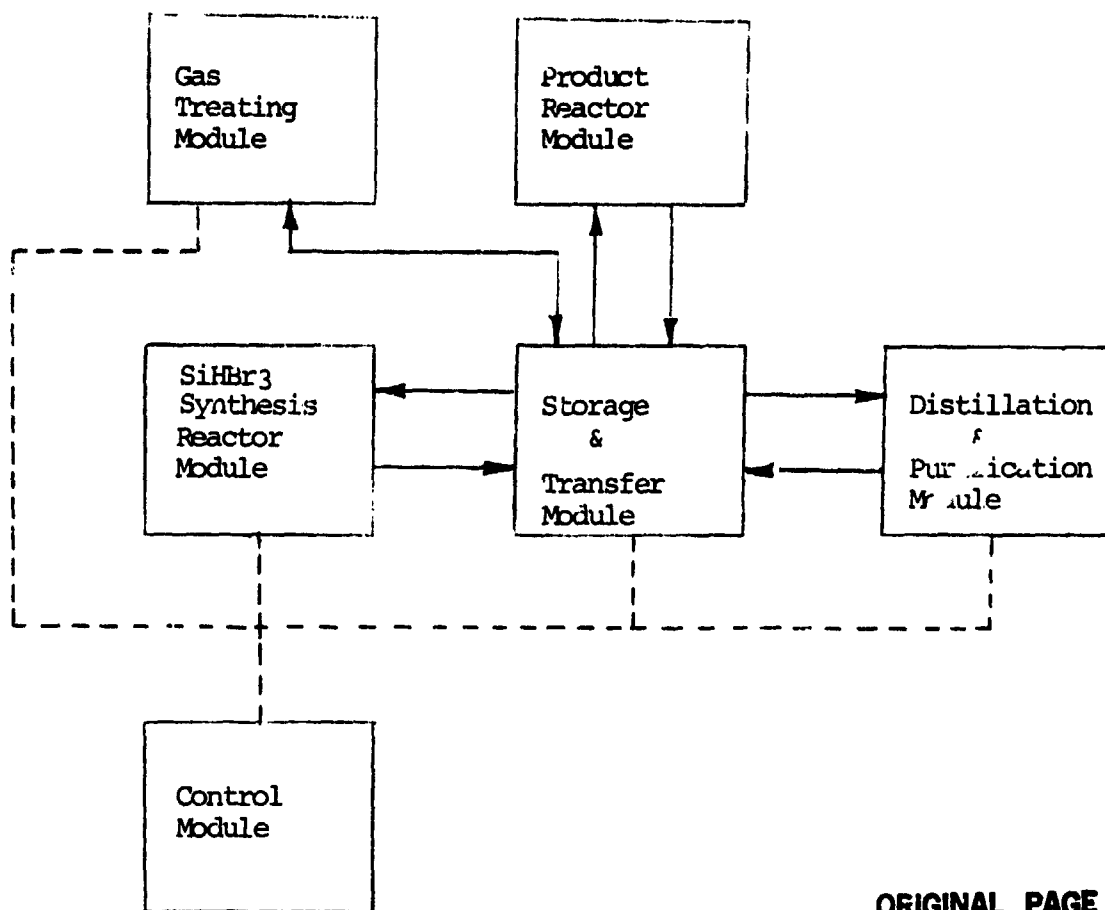
6.2 RECOMMENDATIONS FOR FUTURE DEVELOPMENT

It is suggested that a modular process pilot plant be designed and constructed wherein the individual reactions and purification processes can be demonstrated and characterized. The proposed modular design will allow individual unit operations to be investigated singly or to be integrated into the operations of any other module or group of modules.

The closed-loop nature of the process will be demonstrated, and product silicon will be provided for quality analysis. Other key areas to be investigated or demonstrated include:

- 1) Internal designs for SiHBr_3 synthesis reactor
 - a) HBr process
 - b) SiBr_4 process
 - c) Possible HBr - SiBr_4 combination in single reactor
- 2) Internal designs for Si Production (Thermal decomposition or hydrogen reduction) reactor
- 3) Purification and distillation
 - a) Identification of impurities
 - b) System optimization
- 4) Thermal optimization, including reactor feed-effluent heat exchangers
- 5) Materials of construction
 - a) Product contamination
 - b) Lifetime
- 6) Environmental impact
 - a) Vent gas scrubbing
 - b) Solids disposal
- 7) Gas recycle and separation
 - a) H_2 - HBr separation
 - b) H_2 compression
- 8) Make-up requirements
 - a) Hydrogen
 - b) Bromine species
 - c) Silicon

The proposed pilot plant is shown in Figure 18. It consists of six modular process or control based units.



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FIGURE 18

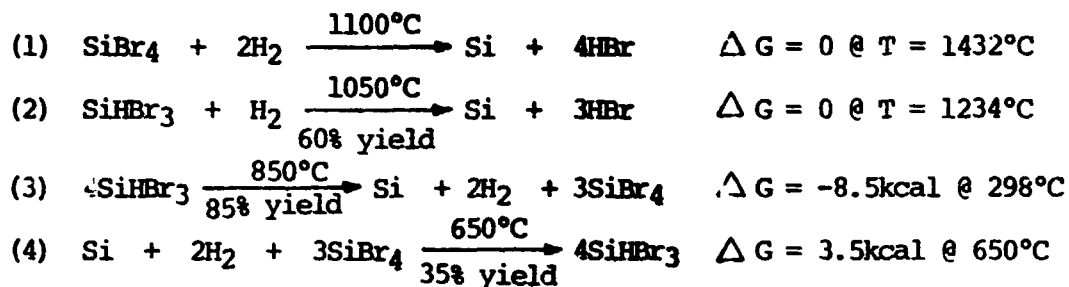
SCHEMATIC BLOCK DIAGRAM OF 1 MT/Y
MODULAR PILOT PLANT FOR SILICON PRODUCTION

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APPENDIX

APPENDIX

During the course of the work performed on JPL Contract 954914 by the J. C. Schumacher Company, observations have been made which appear contrary to published Thermodynamic Properties of Bromosilanes (14). In particular, the following reactions have been seen to occur in appreciable yield at temperatures significantly below T for $\Delta G = 0$ according to (14).



The discrepancy between observed and predicted results can be due to several reasons, among which are

- (1) errors in extrapolated and interpolated data base in (14)
- (2) non-equilibrium conditions in experiments
- (3) side reactions producing a net $\Delta G < 0$ and by-products

It is interesting to note that Sangster (16) predicts the following T for $\Delta G = 0$:



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